Cumulant Expansions and Pressure Broadening as an Example of Relaxation

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Pressure broadening by neutral atoms is treated in a time-dependent formalism making use of generalized cumulants due to Kubo. A thermal-equilibrium initial density matrix is assumed, unlike in previous theories by Baranger and Fano who neglect initial correlations between atoms; it is pointed out that the wings of the spectrum depend in an essential manner on these initial correlations. The treatment centers on a *time-evolution operator* $U(t)=(\mathrm{Tr}_B\rho)^{-1}\times\mathrm{Tr}_B\rho e^{itH^\times}$ operating in the Liouville space of the radiating atom and governing its motion under the influence of the perturbing gas or *bath* $\{\mathrm{Tr}_B$ is the trace over bath coordinates, $\rho\sim e^{-\beta H}$ is the density matrix, and $H^\times$ is the quantum-mechanical Liouvillian: $H^\times(\;)=[H,(\;)]$; H is the total Hamiltonian for the system radiator plus bath$\}$; $U(t)$ is written as $U(t)=T_\rightarrow\exp[i\int_0^t dt'L(t')]$, $L(t)=H_s^\times+R(t)$ ($T_\rightarrow$ is a time-ordering operator), where the effect of the bath is contained in the time-dependent non-Hermitian perturbation $R(t)$ added to the Liouvillian $H_s^\times$ of the unperturbed radiator. The operator $R(t)$ is expanded in powers of a "reduced" density equal to the perturbing-gas density multiplied by the ratio of the fugacities corresponding to mutually interacting and noninteracting perturbing atoms, respectively; the terms of the expansion are expressed by means of generalized cumulants, and describe interactions of the radiator with clusters of perturbers. By setting $R(t)=\bar{R}+\tilde{R}(t)$, where $\bar{R}\equiv\lim_{T\rightarrow\infty}[(1/T)\int_0^T dt\,R(t)]$, the spectrum is written as the sum of its impact approximation, determined by $\bar{R}$, plus a correction expanded in powers of $\tilde{R}(t)$, which to first order in the gas density equals the one-perturber spectrum minus its singularities at the resonance frequencies.

I. INTRODUCTION

Much of the recent work on pressure broadening[1–4] is based on the theory of Fano,[5] whose approach is equivalent to that of Zwanzig[6] for treating relaxation phenomena. Fano[5] assumes that the initial density matrix is a product of two matrices, one for the radiating atom (the system of interest) and one for the gas of perturbing atoms (the *bath*), thus neglecting initial correlations between radiator and perturbers. In reality, there always exist correlations between the particles of a gas, and by neglecting initial correlations, one allows initial states in which different atoms are arbitrarily close to each other and hence have arbitrarily large potential energies; this can significantly affect the radiated spectrum, since this extra available potential energy may be transferred to the radiation field.

In this paper, we assume an initial density matrix which describes thermal equilibrium of the whole system radiator plus perturbers. The exponential form of the equilibrium density matrix allows us to consider it formally as an extension into imaginary times of the Liouville-space time-evolution operator; this brings about considerable simplifications in the notation and in the combinatorial manipulations required to perform the perturbation expansions. But the general procedure used can be applied to the case of arbitrary initial density matrices.

The spectrum is given, as usual,[5,7] by the Fourier transform of the autocorrelation function of the radiating dipole moment. After performing (formally) the trace over bath coordinates, the correlation function is expressed in terms of a nonunitary time-evolution operator $U(t)$ which operates in the Liouville space of the radiator alone. The operator $U(t)$ cannot be calculated exactly in general; furthermore, its perturbation expansions, which can be derived quite straightforwardly, do not converge uniformly with respect to t, and consequently cannot be truncated. One therefore seeks to express $U(t)$ in terms of quantities which have *usable* perturbation expansions. Two different approaches suggest themselves naturally, when one notices that in the absence of the bath, $U(t)=e^{itH_s^\times}$, where $H_s^\times$ is the Liouvillian of the unperturbed radiator, and the Fourier transform of $U(t)$ is $U(\omega)=-i(\omega-i0-H_s^\times)^{-1}$. In the first approach, we write

$$U(t)=T_\rightarrow\exp[i\int_0^t dt'\,L(t')]\;,\quad L(t)=H_s^\times+R(t)\;,\tag{1.1}$$

where $T_\rightarrow$ is a time-ordering operator, and $L(t)$ is the radiator Liouvillian to which is added a time-dependent perturbation $R(t)$ representing the effect of the bath; in other words, to the "frequency" $H_s^\times$ is added a time-dependent part, and since we deal with operators, the exponential is time ordered. In the second approach, we write

$$iU(\omega)=[\omega-H_s^\times-C(\omega)]^{-1}\;,\tag{1.2}$$

in which the effect of the bath is contained in the frequency-dependent $C(\omega)$. In these two approaches, we solve, respectively, for $R(t)$ and $C(\omega)$ in terms of U, and deduce their perturbation expansions, which we expect can be truncated, directly from those of U. In this paper, we shall concentrate mainly on the first approach; a detailed study of the second "resolvent" approach will form the subject of a forthcoming paper.

Much of the paper is devoted to deriving the density expansions of $U(t)$ and $R(t)$. Actually, the expansion parameter is not the gas density itself, but a "reduced" density n equal to the gas density multiplied by the ratio of the fugacities corresponding to mutually interacting and noninteracting perturbing atoms, respectively; a strict density expansion can be obtained by then performing the density expansion of the interacting gas fugacity. The "reduced" density expansion of $R(t)$ is expressed in terms of generalized cumulants due to Kubo,[8] and its terms describe interactions of the radiator with clusters of perturbers.

At large times, $R(t)$ tends to a constant $\bar{R} \equiv \lim_{T\to\infty}[(1/T)\int_0^T dt\, R(t)]$ upon which may be superposed oscillatory terms due to the formation of radiator-perturber bound states; the non-Hermitian operator $\bar{R}$ represents a complex frequency simulated by successive collisional phase shifts. It is $\bar{R}$ which, resulting from the cumulative effect of many collisions, causes the successive terms in the density expansion of $U(t)$ to diverge as increasing powers of t, thus forbidding one to approximate $U(t)$ by truncating its expansion. On the other hand, the oscillating part $\tilde{R}(t) \equiv R(t) - \bar{R}$ represents the effect of perturbers while in close proximity to the radiator, and one may expand $U(t)$ in powers of that quantity, and from this construct a density expansion of the spectrum; the first term of that density expansion is the impact approximation to the spectrum, which is essentially independent of the initial correlations; the second term is the one-perturber spectrum minus its singularities at the resonance frequencies, and it depends in an essential manner on the initial correlations between the radiator and the perturber. Together, these two terms constitute the spectrum in the binary-collision approximation.

In Sec. II, the basic expressions and definitions are given. In Sec. III, the general expressions of $R(t)$ and $C(\omega)$ are derived, and by treating $\tilde{R}(t)$ as a perturbation, the spectrum is written as the sum of its impact approximation plus a correction expanded in powers of $\tilde{R}(t)$. In Sec. IV, some simplifying notation involving imaginary times is introduced. In Sec. V, $R(t)$ is expanded in powers of the radiator-perturber interaction and the result expressed in terms of cumulants.[8] In Sec. VI, cluster expansion methods of the equilibrium theory of fluids[9] are used to expand $U(t)$ in powers of the "reduced" density, and the corresponding expansion of $R(t)$ is then deduced and expressed in terms of cumulants. In Sec. VII, the physical significance and structure of the "reduced" density expansions are discussed. Sections VIII and IX are more specific to pressure broadening, unlike the preceding sections which can apply to a large class of relaxation phenomena; in Sec. VIII, the average over the irrelevant translational motion of the radiator is performed, and in Sec. IX, the spectrum is written to first order in the density, valid in the binary-collision limit.

Throughout this paper, the frequency ω and the time τ are considered conjugate variables in the sense that for any function $f(\tau)$, the function $f(\omega)$ is defined by

$$f(\omega) = \int_0^\infty d\tau\, e^{-i\omega\tau} f(\tau) \;.$$

II. BASIC EXPRESSIONS AND DEFINITIONS

A. Line Shape

Let us consider a radiating atom, the "radiator," immersed in a gas of other atoms, the "perturbers," there being N perturbers in a volume $\mathcal{V}$. The power radiated at the frequency ω is denoted $(4\omega^4/3c^3)\pi^{-1}\,\mathrm{Re}\, I(\omega)$, where c is the velocity of light and Re denotes the real part. $\mathrm{Re}\, I(\omega)$, or simply $I(\omega)$, is referred to as the *spectrum* or *line shape;* it can be expressed[5,7] as the Fourier transform of the autocorrelation function of the radiating dipole moment operator D (units are chosen such that $\hbar = 1$):

$$I(\omega) = \int_0^\infty d\tau\, e^{-i\omega\tau} I(\tau) \;,$$
$$I(\tau) = \mathrm{Tr}\, \rho D(\tau) D = \mathrm{Tr}\, D\rho D(\tau) \;, \tag{2.1}$$

where

$$D(\tau) = e^{i\tau H} D\, e^{-i\tau H} \;,$$

H being the Hamiltonian for the whole system radiator plus perturbers, and

$$\rho = e^{-\beta H}/Z, \quad Z \equiv \mathrm{Tr}\, e^{-\beta H} \;,$$

is the thermal-equilibrium density matrix. Equation (2.1) is rewritten in the form[10]

$$I(\tau) = \mathrm{Tr} D\rho\, e^{i\tau H^\times} D \;, \tag{2.2}$$

where, for any operator A, the Liouville-space operator $A^\times$ is defined by its action on any operator B:

$$A^\times B = AB - BA \;;$$

this notation is due to Kubo[8,11]; $H^\times$ is the quantum-mechanical Liouvillian. Expression (2.2) may be viewed as a correlation function, or alternatively[5] as the average value of $D(\tau)$ when the initial density matrix is $D\rho$, where D represents the effect on ρ of an impulsive interaction with radiation at time zero.

B. Time-Evolution Operator

The underlying physical picture here is that of a small system $\mathcal{S}$, the radiator, in interaction with a large system of very many degrees of freedom, the perturber gas, or *bath* $\mathcal{B}$. We are interested in the correlation or expectation value of operators (the dipole moment) which pertain to $\mathcal{S}$ alone; the bath $\mathcal{B}$ is relevant to our problem only in regard to the influence it has on the state and time evolution of the *observed* system $\mathcal{S}$. As in ordinary quantum mechanics, it is convenient to define an operator $U(\tau)$ which governs the time evolution of the (open) system $\mathcal{S}$ considered; this time-evolution operator can then be studied separately, independently of what are the observables of $\mathcal{S}$ one is interested in.

Inspection of Eq. (2.2) suggests the definition

$$U(\tau) \equiv (\mathrm{Tr}_B\,\rho)^{-1}\,\mathrm{Tr}_B\,\rho\, e^{i\tau H^\times}\,, \quad U(0)=1\,, \qquad (2.3)$$

where Tr_B (Tr_s) denotes the trace over bath (system) coordinates. Then

$$I(\tau) = \mathrm{Tr}_s\, D\sigma U(\tau) D\,, \qquad (2.4)$$

where

$$\sigma \equiv \mathrm{Tr}_B\,\rho\,, \quad \mathrm{Tr}_s\,\sigma = 1$$

is the reduced density matrix describing the state of the radiator at time zero; we note that by the lemma of Appendix C, σ is a function of H_s. Equation (2.4) is of the same form as (2.2), but with the density matrix ρ and the Liouville-space time-evolution operator $e^{i\tau H^\times}$ replaced by corresponding quantities σ and $U(\tau)$ which operate in the space of the radiator alone.

C. Interaction Representation

The time-evolution operator $U(\tau)$ is now expressed in a kind of "interaction representation," which is more practical for performing perturbation expansions. The Hamiltonian H is first written in the form

$$H = H_s + H_B + V = H_0 + V\,,$$

$$H_0 = H_s + H_B\,,$$

where H_s is the Hamiltonian of the radiator alone, and

$$H_B = \sum_{j=1}^{N} H_j$$

is the sum of the one-perturber Hamiltonians; V is the interaction between atoms:

$$V = V_{sB} + V_B = \sum_{j=1}^{N} V_{sj} + \sum_{i<j} V_{ij}\,, \qquad (2.5)$$

where V_{sj} is the interaction between the radiator and the jth perturber, and V_{ij} the interaction between the ith and jth perturbers. In general, it would be more natural to let V be the system-bath interaction alone, but the interperturber interaction V_B is included in V for convenience in the later expansion into powers of the gas density.[5]

The following density matrices are now defined:

$$\rho_s \equiv e^{-\beta H_s}/Z_s\,, \quad Z_s \equiv \mathrm{Tr}_s\, e^{-\beta H_s}\,;$$

$$\rho_B \equiv e^{-\beta H_B}/Z_B\,, \quad Z_B \equiv \mathrm{Tr}_B\, e^{-\beta H_B}\,.$$

Using the fact that H_B commutes with H_s and with operators which pertain to the radiator alone (so that $H_B^\times D = 0$), we can write Eq. (2.2) in the form

$$I(\tau) = \mathrm{Tr}_s\, D\rho_s\, B(\tau)\, e^{i\tau H_s^\times} D\,, \qquad (2.6)$$

where

$$B(\tau) \equiv \rho_s^{-1}\,(\mathrm{Tr}_B\,\rho\, e^{i\tau H^\times})\, e^{-i\tau H_s^\times}$$

$$= (Z_s Z_B/Z)\,\mathrm{Tr}_B\,\rho_B (e^{\beta H_0}\, e^{-\beta H})$$

$$\times (e^{i\tau H^\times}\, e^{-i\tau H_0^\times})\,. \qquad (2.7)$$

The *bath operator* $B(\tau)$ contains all the effect of the bath on the radiator, and it would equal 1 if the radiator and bath did not interact[12]; at $\tau = 0$, $B(\tau)$ consists of an impulsive interaction $B(0) = \rho_s^{-1}\sigma$, which changes the initial-density matrix of the radiator from ρ_s, what it would be in the absence of the bath, to σ, its actual form. As τ increases, $B(\tau)$ describes the effect of the bath on the subsequent evolution of the radiator.

The bath operator $B(\tau)$ can be expanded straightforwardly into powers of the system-bath interaction strength, which may be taken as V_{sB}, or as the perturbing gas density, which determines the *average* strength of the interaction. All quantities of interest will be expressed in terms of $B(\tau)$, and their perturbation expansions deduced directly from those of $B(\tau)$.

In terms of $B(\tau)$, the time-evolution operator $U(\tau)$ has the expression

$$U(\tau) = B(0)^{-1}\, B(\tau)\, e^{i\tau H_s^\times}\,. \qquad (2.8)$$

III. GENERAL TREATMENT

A. Equation of Motion for $U(t)$

The time-evolution operator $U(t)$ satisfies the (trivial) equation

$$\frac{d}{dt}\, U(t) \equiv \dot{U}(t) = U(t)\,[U(t)^{-1}\,\dot{U}(t)]\,;$$

this can be rewritten (note that $H_s^\times$ is the value of $U^{-1}\dot{U}$ in the absence of the bath):

$$\frac{d}{dt}\, U(t) = iU(t)\,[H_s^\times + R(t)]\,, \quad U(0) = 1, \qquad (3.1)$$

where

$$R(t) \equiv (1/i)\, U(t)^{-1}\, \dot{U}(t) - H_s^\times$$

contains the effect of the bath on the evolution of the system. In terms of $B(t)$, $R(t)$ has [by Eq. (2.8)] the expression

$$R(t)=(1/i)\, e^{-itH_s^\times} B(t)^{-1}\, \dot{B}(t)\, e^{itH_s^\times} \tag{3.2}$$

from which the perturbation expansions of $R(t)$ can be deduced from those of $B(t)$.

For future reference, we note that

$$\begin{aligned} &\frac{d}{dt} B(t)=iB(t)\,\hat{R}(t)\,, \\ &\hat{R}(t)\equiv e^{itH_s^\times} R(t)\, e^{-itH_s^\times}\,. \end{aligned} \tag{3.3}$$

B. Solutions

Equation (3.1) has the formal solution (1.1), in which $T_{\rightarrow}$ ($T_{\leftarrow}$) orders operators such that their time arguments increase from left to right (right to left).

The operator $R(t)$ will be seen to tend to a constant as $t\rightarrow\infty$, on which may be superposed oscillatory terms due to the possible existence of bound states between the radiator and perturbers; we may accordingly write

$$R(t)=\bar{R}+\tilde{R}(t)\,, \tag{3.4}$$

where

$$\bar{R}\equiv \lim_{T\rightarrow\infty} T^{-1}\int_0^T dt\, R(t)$$

is the average value of $R(t)$, and

$$\tilde{R}(t)\equiv R(t)-\bar{R}$$

is an "oscillating" term which reflects, at small values of t, the details of the time evolution during radiator-perturber collisions, in addition to containing the long-lived oscillations due to bound states.

An expression of $U(\tau)$ more useful than (1.1) can now be obtained by treating $\tilde{R}(t)$ as a "perturbation" added to the time-independent operator

$$\mathcal{L}\equiv H_s^\times+\bar{R}$$

in Eq. (3.1); setting

$$\tilde{R}_t(t)\equiv e^{it\mathcal{L}}\, \tilde{R}(t)\, e^{-it\mathcal{L}}\,,$$

we have

$$\begin{aligned} U(\tau)&=T_{\rightarrow} \exp\Big[i\int_0^\tau dt\, \tilde{R}_t(t)\Big]\, e^{i\tau\mathcal{L}} \\ &=e^{i\tau\mathcal{L}}+i\int_0^\tau dt\, e^{it\mathcal{L}}\, \tilde{R}(t)\, e^{i(\tau-t)\mathcal{L}} \\ &\quad+i^2\int_0^\tau dt\int_0^t dt'\, e^{it'\mathcal{L}}\, \tilde{R}(t') \\ &\quad\times e^{i(t-t')\mathcal{L}}\, \tilde{R}(t)\, e^{i(\tau-t)\mathcal{L}}+\cdots\,. \end{aligned} \tag{3.5}$$

One may interpret this expansion as a sum over histories in the usual manner, with an "interaction" $\tilde{R}(t)$, and an "unperturbed" time-evolution operator $e^{it\mathcal{L}}$ governing the "average" motion of the radiator in the bath.

Let τ_c be a time such that when $t>\tau_c$, $R(t)$ essentially assumes its asymptotic value $\bar{R}$ (here we neglect the possibility of radiator-perturber bound states), or equivalently, $U(t)$ essentially equals $A\, e^{it\mathcal{L}}$, where

$$A\equiv T_{\rightarrow} \exp\Big[i\int_0^\infty dt\, \tilde{R}_t(t)\Big]\,. \tag{3.6}$$

In the binary-collision limit, τ_c would be the mean duration of a collision. The asymptotic value of $U(\tau)$ determines $U(\omega)$ in the vicinity $|\omega-\omega_s|\ll\tau_c^{-1}$ of resonance frequencies ω_s, namely, $U(\omega)=-iA(\omega-\mathcal{L})^{-1}$; this yields the impact spectrum

$$I_{\mathrm{imp}}(\omega)=-i\,\mathrm{Tr}_s\, D\sigma A(\omega-\mathcal{L})^{-1} D\,. \tag{3.7}$$

The non-Hermitian operator A introduces a skewness into the Lorentzian line shape, in addition to that arising from the interference of overlapping lines[7]; it is usually treated to lowest order in the density, i.e., set equal to 1. In the adiabatic theory of pressure broadening, the counterpart of A is well known and its main effect is to produce an asymmetry in the line.[13]

The operator $U(\tau)$ may be written

$$U(\tau)=A\, e^{i\tau\mathcal{L}}+A\, N(\tau)\,, \tag{3.8}$$

where[14]

$$N(\tau)=\Big\{T_{\leftarrow}\exp\Big[-i\int_\tau^\infty dt\, \tilde{R}_t(t)\Big]-1\Big\}\, e^{i\tau\mathcal{L}}\ ;$$

thus

$$U(\omega)=-iA(\omega-\mathcal{L})^{-1}+A\, N(\omega)\,. \tag{3.9}$$

It will be seen in Sec. IX that to first order in the gas density, $AN(\omega)$ yields the one-perturber spectrum to which are substracted its singularities at the resonance frequencies.

C. Resolvent Form

Rather than include the effect of the bath in a time-dependent perturbation added to the system Liouvillian, we may also introduce it as a frequency-dependent operator added to $H_s^\times$ in the unperturbed resolvent $-i(\omega-i0-H_s^\times)^{-1}$; this form, which is that obtained in Fano's theory,[5] is now briefly discussed (in this section, the frequency ω is understood to have a small negative imaginary part $-i0$).

Let us set

$$iU(\omega)=[\omega-H_s^\times-C(\omega)]^{-1}\ ; \tag{3.10}$$

solving for $C(\omega)$, we have

$$\begin{aligned} C(\omega)&=\omega-H_s^\times-[iU(\omega)]^{-1} \\ &=\left(1-\frac{1}{i(\omega-H_s^\times)U(\omega)}\right)\,(\omega-H_s^\times)\,. \end{aligned} \tag{3.11}$$

We introduce the quantity

$$\langle M(\omega)\rangle\equiv(\omega-H_s^\times)\,[iU(\omega)-(\omega-H_s^\times)^{-1}]\,(\omega-H_s^\times)\,, \tag{3.12}$$

which vanishes as the system-bath interaction tends to zero, since it is proportional to $iU(\omega)$ minus its value $(\omega - H_s^\times)^{-1}$ in the absence of the bath. We then have

$$C(\omega) = \left(1 - \frac{1}{1 + \langle M(\omega)\rangle (\omega - H_s^\times)^{-1}}\right)(\omega - H_s^\times)$$

$$= \frac{1}{1 + \langle M(\omega)\rangle (\omega - H_s^\times)^{-1}} \langle M(\omega)\rangle , \qquad (3.13)$$

which is Fano's[5] Eq. (20), but without any assumptions on the density matrix. The operator $\langle M(\omega)\rangle$ also has the expression

$$\langle M(\omega)\rangle = i(\omega - H_s^\times)\int_0^\infty d\tau \,[B(0)^{-1}B(\tau) - 1]$$

$$\times e^{-i\tau(\omega - H_s^\times)}(\omega - H_s^\times) , \qquad (3.14)$$

which may be used to deduce the perturbation expansion of $\langle M(\omega)\rangle$ and hence that of $C(\omega)$ from the expansion of $B(\tau)$. To first order in the density, $C(\omega)$ and $\langle M(\omega)\rangle$ are equal [by (3.13)] and given by the right-hand side of (3.14), with $B(0)$ replaced by unity and $B(\tau)$ by its first-order approximation. This first-order expression for $C(\omega)$ (but with $\rho = \rho_s\rho_B$) is used by Smith *et al.*[3] as a starting point for numerical calculations.[15]

An alternate expression of $U(\omega)$ is obtained by setting

$$iU(\omega) = [\omega - \mathcal{L} - D(\omega)]^{-1} \qquad (3.15)$$

in which the operator $D(\omega)$ vanishes with $\tilde{R}(t)$; using Eq. (3.9), we obtain

$$D(\omega) = (\omega - \mathcal{L})\left(1 - \frac{1}{1 + iN(\omega)(\omega - \mathcal{L})} A^{-1}\right)$$

$$= (\omega - \mathcal{L})\{(1 - A^{-1}) - \sum_{k=1}^{\infty}[-iN(\omega)(\omega - \mathcal{L})]^k A^{-1}\} . \qquad (3.16)$$

We note that Eq. (3.15) implies the following non-Markoffian equation for $U(\tau)$:

$$\frac{d}{dt}U(\tau) = iU(\tau)\mathcal{L} + i\int_0^\tau dt\, U(t)\, D(\tau - t) ,$$

$$U(0) = 1 . \qquad (3.17)$$

With reference to Eq. (3.17) we may speak of $D(\omega)$, or $N(\omega)$, or $\tilde{R}(t)$, as representing the *non-Markoffian* effects, and of $(\omega - \mathcal{L})^{-1}$ as being the *Markoffian* approximation to $iU(\omega)$; but this distinction is somewhat artificial since $U(\tau)$ also satisfies the Markoffian Eq. (3.1).

IV. COMPLEX-TIME NOTATION

In order to simplify the manipulations required to perform its perturbation expansions, the bath operator $B(\tau)$ will now be written in a compact form by taking advantage of the exponential nature of the equilibrium-density matrix and considering it as an extension into imaginary times of the time-evolution operator.

We first rewrite expression (2.7) of $B(\tau)$ in the form

$$B(\tau) = (Z_s Z_B/Z)\,\mathrm{Tr}_B\,\rho_B\, T_{\leftarrow b}\exp[-\int_0^\beta db\, V(-ib)]$$

$$\times\, T_{t\rightarrow}\exp[i\int_0^\tau dt\, V(t)^\times] , \qquad (4.1)$$

where

$$V(-ib) \equiv e^{bH_0}\,Ve^{-bH_0} = e^{i(-ib)H_0}\,Ve^{-i(-ib)H_0} ,$$

$$V(t) \equiv e^{itH_0}\,Ve^{-itH_0} .$$

[note that for any two operators A and B: $e^{\times} Be^{-A\times} = e^A Be^{-A}$, $e^{A^\times}B^\times e^{-A^\times} = (e^A Be^{-A})^\times$; thus $e^{itH_0^\times}V^\times e^{-itH_0^\times} = (e^{itH_0}Ve^{-itH_0})^\times = V(t)^\times$]; the operator $T_{t\rightarrow}$ orders the $V(t)^\times$ such that their time arguments increase from left to right, and $T_{\leftarrow b}$ orders the $V(-ib)$ such that the arguments b increase from right to left. Defining the operation $T_{\leftarrow b,t\rightarrow}$ which compounds the two previous operations in addition to putting all $V(-ib)$ to the left of all $V(t)^\times$, we also have

$$B(\tau) = (Z_s Z_B/Z)\,\mathrm{Tr}_B\,\rho_B\, T_{\leftarrow b,t\rightarrow}$$

$$\times \exp[-\int_0^\beta db\, V(-ib) + i\int_0^\tau dt\, V(t)^\times] .$$

Another, more suggestive, form is obtained by defining the complex-time variable $z = t + ib$, and the function

$$W(z) \equiv V(z)^\times = V(t)^\times \text{ on the real } z \text{ axis}$$

$$\equiv V(z) = V(t + ib) \text{ off the real axis} , \qquad (4.2)$$

where

$$V(z) \equiv e^{izH_0}\,Ve^{-izH_0} . \qquad (4.3)$$

We then write

$$B(\tau) = (Z_s Z_B/Z)\,\mathrm{Tr}_B\,\rho_B\, T_{z\rightarrow}\exp[i\int_{-i\beta}^\tau dz\, W(z)] , \qquad (4.4)$$

where $\int_{-i\beta}^\tau dz$ denotes the integral along the contour shown in Fig. 1, namely, from $-i\beta$ to 0 along the imaginary z axis, and then from 0 to τ along the real axis; the operation $T_{z\rightarrow}$ orders the $W(z)$ such that when read from left to right, the arguments z proceed from $-i\beta$ to τ along the contour.

It will prove convenient to define the operation

$$\langle \cdots \rangle \equiv \mathrm{Tr}_B\,\rho_B\, T_{z\rightarrow}(\cdots) , \quad \langle 1 \rangle = 1 , \qquad (4.5)$$

which contains the complex-time-ordering operation in addition to that of averaging over the bath variables. Then

$$B(\tau) = (Z_s Z_B/Z)\langle \exp[i\int_{-i\beta}^\tau dz\, W(z)]\rangle . \qquad (4.6)$$

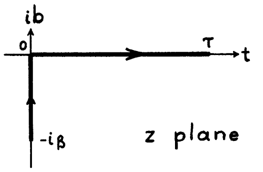

FIG. 1. Complex-time integration contour defining $\int_{-i\beta}^\tau dz$.

In expressions (4.4) and (4.6), we may consider $-i\beta$ as representing an "initial time" at which the particles of the gas, radiator, and perturbers, are uncorrelated, i.e., the density matrix is a product of one-particle density matrices; as time proceeds along the imaginary axis from $-i\beta$ to 0, the particles "interact" thus building up the correlations contained in the density matrix at the *physical* initial time zero; time then proceeds along the positive real axis. The complex-time-ordered exponentials may be expanded and interpreted in terms of Feynman diagrams, with interactions occurring at imaginary times influencing the initial state (at time zero) of the radiator, and those occurring at real times affecting its subsequent evolution.

From expression (4.1), it is seen that $B(\tau)$ tends to zero as $\tau\to\infty$, for as τ increases, the possible values of the phase $\int_0^\tau dt\, V(t)^\times$ become more and more spread out, so that the average of its exponential tends to vanish.

V. EXPANSION IN POWERS OF THE INTERACTION V

The operator $R(t)$ has been introduced as a quantity which, unlike $U(\tau)$ or $B(\tau)$, is expected to have perturbation expansions that converge uniformally with respect to t, and can therefore be used as a basis for eventual approximations. The expansion parameter will usually be the strength of the system-bath interaction, which can be taken directly as the interaction V, or alternatively as the perturbing gas density, which determines the average strength of the interaction. The expansion in powers of V is of more general applicability, and is briefly treated in this section; the density expansion, which is of use only if the bath is a gas, as in our problem, is derived in Sec. VI.

In order to obtain the expansion of $R(t)$ into powers of the interaction V, one must introduce (4.6) into (3.2), and expand the result into powers of V. But actually, the expansion of the logarithm of an expression of the type (4.6), namely, the average of an exponential function, defines well-known combinatorial objects called *cumulants;* Kubo[8] has extended the theory of cumulants to include time-ordered exponentials, and the explicit expressions and properties of the cumulants of the type we use are given in Appendix A.

In terms of cumulants, we can immediately write

$$\begin{aligned}B(\tau)&=(Z_sZ_B/Z)\,T_{z\to}\exp[i\int_{-i\beta}^{\tau}dz\,\hat{R}(z)]\\&=\{(Z_sZ_B/Z)\,T_{z\to}\exp[i\int_{-i\beta}^{0}dz\,\hat{R}(z)]\}\\&\qquad\times T_{t\to}\exp[i\int_0^{\tau}dt\,\hat{R}(t)]\\&=B(0)\,T_{t\to}\exp[i\int_0^{\tau}dt\,\hat{R}(t)]\ ,\end{aligned}\tag{5.1}$$

where

$$\hat{R}(z)=\langle\exp[i\int_{-i\beta}^{z}dz'\,W(z')]\,W(z)\rangle_{c\to}\ ,\tag{5.2}$$

and the cumulant average $\langle\ \rangle_{c\to}$ is defined in Appendix A. We thus have, according to Eq. (3.3),

$$\begin{aligned}e^{itH_s^\times}R(t)\,e^{-itH_s^\times}=\hat{R}(t)&=\langle\exp[i\int_{-i\beta}^{t}dz'\,W(z')]\;V(t)^\times\rangle_{c\to}\\&=e^{itH_s^\times}\langle\exp[i\int_{-i\beta}^{t}dz'\,W(z'-t)]\,V^\times\rangle_{c\to}\,e^{-itH_s^\times}\ ;\end{aligned}\tag{5.3}$$

in time translating by $-t$ all operators in the cumulant bracket, we have used the relation

$$\begin{aligned}\langle\textstyle\prod_i W(z_i)\rangle&=\langle e^{itH_0^\times}(\textstyle\prod_i W(z_i-t))\,e^{-itH_0^\times}\rangle\\&=e^{itH_s^\times}\langle\textstyle\prod_i W(z_i-t)\rangle\,e^{-itH_s^\times}\ ,\end{aligned}$$

the second equality following from the fact that H_s and H_B commute with ρ_B, so that the operators $e^{\pm itH_B^\times}$ cancel each other by the cyclic property of the trace Tr_B [recall $H_0=H_s+H_B$, and the definition (4.5) of the operation $\langle\ \rangle$]. We have finally

$$\begin{aligned}R(t)&=\langle\exp[i\int_{-i\beta}^{t}dz\,W(z-t)]\,V^\times\rangle_{c\to}\\&=\langle V\rangle^\times+i\int_{-i\beta}^{t}dz\,[\langle W(z-t)\,V^\times\rangle\\&\quad-\langle W(z-t)\rangle\langle V^\times\rangle]+\cdots\\&\quad+i^k\int_{-i\beta}^{t}dz_1\int_{-i\beta}^{z_1}dz_2\cdots\int_{-i\beta}^{z_{k-1}}dz_k\\&\quad\times\langle W(z_k-t)\,W(z_{k-1}-t)\cdots\\&\quad\times W(z_1-t)\,V^\times\rangle_{c\to}+\cdots\ .\end{aligned}\tag{5.4}$$

If it can be assumed that *successive* interactions $W(z)$ are statistically uncorrelated when separated in real time by more than some correlation time τ_c, then theorem (A1) of Appendix A implies that the kth-order cumulant in expansion (5.4) vanishes when its two extreme interactions are separated by more than $k\tau_c$ (for then there is at least one time interval larger than τ_c between two successive interactions, which separates the k interactions into two uncorrelated groups). In passing from $\hat{R}(t)$ to $R(t)$, the interactions have been time translated such that the *last* interaction always occurs at time zero, and all the interactions must therefore be clustered near that time. Thus nothing is added to the multiple time integral in Eq. (5.4) when t increases beyond $k\tau_c$; in other words, the kth term of the expansion becomes independent of time after $t=k\tau_c$, and it is therefore concluded that $R(t)$ tends asymptotically to a definite limit.

The above discussion[8] is based on the assumption of a finite correlation time between successive interactions; whether this is the case or not is in general not easy to establish with certainty, though intuitively it seems a reasonable assumption; but one can exhibit cases where a correlation can exist between two successive interactions separated by any amount of time, as will be seen in Sec. VIII when discussing center-of-mass motion of the radiator. The expansion in powers of the density will provide a much sounder basis for discussing the behavior of $R(t)$.

We note that V is the sum of radiator-perturber and perturber-perturber interactions, as defined initially in Sec. II; but we may also think of V as being only the system-bath interaction V_{sB}, and of H_B as being the *total* Hamiltonian for the bath. This latter definition of V is of wider applicability than the one we have chosen, which is really useful only when a density expansion is intended.

VI. EXPANSION INTO POWERS OF THE GAS DENSITY

The radiator immersed in the perturbing gas suffers collisions with individual perturbers or with clusters of perturbers; the interaction between atoms during collisions can be so strong as to preclude treating it as a perturbation, as in Sec. V. If, however, the perturbing-gas density is low enough, collisions may be sufficiently unfrequent as to render the *average* interaction of the radiator with the bath small, in which case the gas density recommends itself as an expansion parameter. But independently of these considerations, the density expansion of $R(t)$, besides providing an approximation scheme, is the most natural way of expressing $R(t)$ in order to reveal its *physical* structure; indeed, the successive terms in the density expansion of $R(t)$ correspond to collisions of the radiator with clusters of perturbers of increasing size, and thus represent the elementary physical processes by which the radiator interacts with the bath.

In order to perform the density expansion, we shall use graph methods of the type used in the equilibrium theory of classical fluids,[9] and the relevant definitions and lemmas are grouped in Appendix B.

A. Expression of $B(\tau)$ in Terms of Labeled Graphs

Referring to the respective definitions (2.5) and (4.2) of V and $W(z)$, we can write

$$W=\sum_{j=1}^{N} W_{sj}+\sum_{i<j} W_{ij}=\sum_{\mu<\nu} W_{\mu\nu}\ , \tag{6.1}$$

where μ and ν take the values $s, 1, 2, \ldots, N$, and for notational convenience we put "$s<1$." Defining

$$f_{\mu\nu}\equiv \exp[i\int_{-i\beta}^{\tau} dz\ W_{\mu\nu}(z)]-1\ , \tag{6.2}$$

we have

$$F(\tau)\equiv \exp[i\int_{-i\beta}^{\tau} dz\ W(z)]=\prod_{\mu<\nu}(f_{\mu\nu}+1)\ . \tag{6.3}$$

According to Eq. (4.6),

$$B(\tau)=(Z_s Z_B/Z)\langle F(\tau)\rangle\ . \tag{6.4}$$

Note that the time-ordering operator included in the operation $\langle\ \rangle$ entangles together the different factors $f_{\mu\nu}$ in a product.

Expression (6.3) is of a form familiar in the theory of the virial expansion for real gases,[9] and we shall make use of the same graphical methods to represent products of $f_{\mu\nu}$'s: we draw a white circle labeled s representing the radiator, and a black circle labeled j to represent the jth perturber; a factor $f_{\mu\nu}$ in a product is then represented by a black line joining the circles representing the μth and νth particles. An example is given in Fig. 2; note that a graph can be viewed and written as the product of its connected parts. In terms of these *labeled* graphs, Eq. (6.3) is written

$$F(\tau)=\text{sum of all distinct labeled graphs.} \tag{6.5}$$

B. Elimination of Graph Components Not Connected to Radiator

Clearly, the radiator is affected only by perturbers which are "connected" to it; we therefore seek to isolate graph components not connected to the radiator by first rewriting the sum (6.5) over all graphs as follows:

$$F(\tau)=\Gamma(s)\,\Xi^{(s)}+\sum_{j=1}^{N}\Gamma_{\text{conn}}(s,j)\,\Xi^{(s,j)}+\sum_{i<j}[\sum\Gamma_{\text{conn}}(s,i,j)]\,\Xi^{(s,i,j)}+\cdots,$$

where $\Gamma(s)$ is the graph consisting of the radiator alone, and $\Xi^{(s)}$ is the sum of *all* graphs *not* containing the radiator, and $\sum\Gamma_{\text{conn}}(s,i,j,\ldots)$ is the sum of all *connected* graphs containing circles $s, i, j, \ldots,$ while $\Xi^{(s,i,j,\ldots)}$ is the sum of *all* graphs *not* containing $s, i, j, \ldots$. In other words,

$$F(\tau)=\sum_{m=0}^{N}\ \sum_{j_1<j_2<}\sum\cdots\sum_{<j_m}[\sum\Gamma_{\text{conn}}(s,j_1,\ldots,j_m)]\times\prod_{\mu<\nu}^{(s,j_1,\ldots,j_m)}(f_{\mu\nu}+1)\ , \tag{6.6}$$

where the product $\prod_{\mu<\nu}^{(s,j_1,\ldots,j_m)}$ is over all values of μ and ν to the exclusion of $s, j_1, \ldots, j_m$, and $\sum\Gamma_{\text{conn}}(s,j_1,\ldots,j_m)$ is the sum of all distinct connected labeled graphs of vertices $s, j_1, \ldots, j_m$; for instance,

$$\sum\Gamma_{\text{conn}}(s,i,j)=f_{si}f_{ij}+f_{sj}f_{ij}+f_{si}f_{sj}+f_{si}f_{sj}f_{ij}$$

is represented graphically in Fig. 3.

Because the quantities $\prod_{\mu<\nu}^{(s,j_1,\ldots,j_m)}(f_{\mu\nu}+1)$ and $\sum\Gamma_{\text{conn}}(s,j_1,\ldots,j_m)$ depend on mutually exclusive sets of atoms, the average $\langle\ \rangle$ of their product equals the product of their averages; we then have, assuming all perturbers to be identical,

$$F(\tau)=\sum_{m=0}^{N}[N!/(N-m)!\,m!]$$

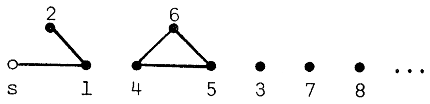

FIG. 2. Labeled graph representing the product $f_{s1}f_{12}f_{45}f_{56}f_{46}\cdots$

$$\times\langle\sum\Gamma_{\text{conn}}(s,\ 1,\ldots,m)\rangle\langle F(\tau)\rangle^{(s,\{m\})}, \tag{6.7}$$

where $\langle F(\tau)\rangle^{(s,\{m\})}\equiv\langle\prod_{\mu<\nu}^{(s,1,\ldots,m)}(f_{\mu\nu}+1)\rangle$; by comparing with (6.3), we see that $\langle F(\tau)\rangle^{(s,\{m\})}$ equals the function $\langle F(\tau)\rangle$, but with the coordinates of the radiator and of m perturbers deleted. Thus [cf. Eqs. (6.4) and (2.7)]:

$$\langle F(\tau)\rangle^{(s,\{m\})}=[\mathrm{Tr}_B\,\rho_B\,e^{\beta H_B}\,e^{-\beta H_B^{(T)}}\,e^{i\tau H_B^{(T)\times}}\,e^{-i\tau H_B^{\times}}]_{(N-m)}$$
$$=[Z_B^{(T)}/Z_B]_{(N-m)},$$

where $H_B^{(T)}\equiv H_B+V_B$ is the total bath Hamiltonian, $Z_B^{(T)}\equiv\mathrm{Tr}_B\exp(-\beta H_B^{(T)})$, and the subscript $(N-m)$ on the square brackets indicates that all quantities inside refer to the perturber gas minus m perturbers; the operators $H_B^{(T)\times}$ and $H_B^{\times}$ have vanished since nothing on their right-hand side depends on the perturber coordinates.

Now, $[Z_B]_{(N-m)}=Z_1^{N-m}$, where $Z_1\equiv\mathrm{Tr}_1\,e^{-\beta H_1}$ is the partition function for a single perturber, and

$$[Z_B^{(T)}]_{(N-m)}=[Z_B^{(T)}]_{(N)}\,e^{m\beta\mu}, \tag{6.8}$$

where μ is the chemical potential for the perturber gas; (6.8) follows from the fact that $N\gg m$, and the relation

$$\frac{\partial}{\partial N}\ln[Z_B^{(T)}]_{(N)}=-\beta\mu .$$

Thus, taking the limit $N\to\infty$, $\mathcal{V}\to\infty$ ($\mathcal{V}$ is the containing volume) with $N/\mathcal{V}=n_B$, the density of the perturber gas, we obtain:

$$B(\tau)=(Z_s Z_B^{(T)}/Z)\sum_{k=0}^{\infty}(n^k/k!)$$
$$\times{}_\infty\langle\mathcal{V}^k\sum\Gamma_{\text{conn}}(s,\ 1,\ 2,\ldots,k)\rangle, \tag{6.9}$$

where the operation

$${}_\infty\langle\cdots\rangle\equiv\lim\langle\cdots\rangle=\lim\mathrm{Tr}\rho_B\,T_{\to}\cdots$$
$$\text{as } \mathcal{V}\to\infty \tag{6.10}$$

and

$$n\equiv n_B\,(Z_1\,e^{\beta\mu})=n_B\,(Z_1/Z_1^{(T)}),$$

where $Z_1^{(T)}\equiv e^{-\beta\mu}=[Z_B^{(T)}]_{(N)}/[Z_B^{(T)}]_{(N-1)}$ is the inverse *fugacity* for the perturber gas; note that Z_1^{-1} is the fugacity of the "noninteracting" perturber gas.
We observe that since the interatomic interactions are assumed of short range, the *connected* graphs $\Gamma_{\text{conn}}(s,\ 1,\ldots,k)$ are of order[16] $\mathcal{V}^{-k}$, so that ${}_\infty\langle\mathcal{V}^k\,\Gamma_{\text{conn}}(s,\ 1,\ldots,k)\rangle$ is well defined.

The expansion (6.9), and all "density expansions" derived in the sequel, are in powers of the "reduced" density n; in order to obtain expansions in powers of the density n_B, n must be expanded in powers of n_B in these expansions $[n=n_B(1+an_B+\cdots)]$. Over-all multiplicative constants in $B(\tau)$ (e.g., $Z_s Z_B^{(T)}/Z$) play no role, and we shall omit writing them in future.

C. Expression of $B(\tau)$ in Terms of Irreducible Graphs

We could now obtain the density expansion of $R(t)$ by introducing (6.9) in (3.2) and expanding the result in powers of n; but it is more enlightening to first make use of a well-known lemma of graph theory[9] and write the sum (6.9) as the average of an exponential function, so that we can then make use of cumulants to obtain $R(t)$.

It is convenient to first attach a weight $n\mathcal{V}$ to each black circle (i.e., perturber) in the connected graphs $\Gamma_{\text{conn}}(s,\ 1,\ldots,k)$ so as to absorb the factors $n^k\mathcal{V}^k$ in expansion (6.9); from now on then, all graphs are understood to be "weighted" graphs in the above sense. By the lemmas (B2) and (B3) of Appendix B, Eq. (6.9) becomes

$$B(\tau)={}_\infty\langle\sum\Gamma_{\text{conn}}/\sigma(\Gamma_{\text{conn}})\rangle$$
$$={}_\infty\langle\exp[\textstyle\sum'\Gamma_{\text{irr}}/\sigma(\Gamma_{\text{irr}})]\rangle, \tag{6.11}$$

where the graphs here are *unlabeled* graphs; the symmetry numbers $\sigma(\Gamma)$ and the irreducible graphs Γ_{irr} are defined in Appendix B. The sums $\sum\Gamma$ are always over all distinct graphs of the type indicated, consisting of one white and some or no black circles, except for the sum $\sum'\Gamma$ which excludes the graph consisting of the white circle (i.e., the radiator) alone.

In order to simplify notation, we define primed graphs

$$\Gamma'\equiv\Gamma/\sigma(\Gamma);$$

then

$$B(\tau)={}_\infty\langle\sum\Gamma'_{\text{conn}}\rangle={}_\infty\langle\exp[\textstyle\sum'\Gamma'_{\text{irr}}]\rangle . \tag{6.12}$$

D. Density Expansion of $R(t)$

We can now write

$$B(\tau)=T_{z\to}\exp\left[\int_{-i\beta}^{\tau}dz\left(\frac{d}{dz}\right)_{\to}\right.$$

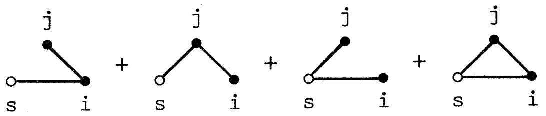

FIG. 3. $\sum\Gamma_{\text{conn}}(s,i,j)$.

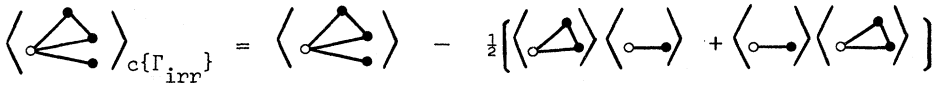

FIG. 4. Example of a $c\{\Gamma_{\mathrm{irr}}\}$ cumulant.

$$\times\, {}_{\infty}\langle \exp[\textstyle\sum' \Gamma'_{\mathrm{irr}}(z)]\rangle_{c\{\Gamma_{\mathrm{irr}}\}}\Big] , \quad (6.13)$$

where the graphs $\Gamma(z)$ have bonds $f_{\mu\nu}(z) \equiv \exp[i\int_{-i\beta}^{z} dz'\, W(z')] - 1$, and $c\{\Gamma_{\mathrm{irr}}\}$ indicates cumulants constructed on the irreducible graphs: For instance,

$$\langle f_{s1} f_{s2} f_{12} f_{s3}\rangle_{c\{\Gamma_{\mathrm{irr}}\}} = \langle f_{s1} f_{s2} f_{12} f_{s3}\rangle$$

$$-\tfrac{1}{2}\,(\langle f_{s1} f_{s2} f_{12}\rangle \langle f_{s3}\rangle + \langle f_{s3}\rangle\langle f_{s1} f_{s2} f_{12}\rangle)$$

is represented graphically in Fig. 4; the operation $(d/dz)_{\rightarrow}$, defined in Appendix A, equals the ordinary differential operator (d/dz), with the difference that when operating on a product, each differentiated factor is displaced to the right of all other factors.

We thus again have Eq. (5.1), this time with

$$\hat{R}(t) = (1/i)\left(\frac{d}{dt}\right)_{\rightarrow} {}_{\infty}\langle \exp[\textstyle\sum' \Gamma'_{\mathrm{irr}}(t)]\rangle_{c\{\Gamma_{\mathrm{irr}}\}} \quad (6.14)$$

$$= (1/i)\left(\frac{d}{dt}\right)_{\rightarrow} {}_{\infty}\langle \textstyle\sum \Gamma'_{\mathrm{conn}}(t)\rangle_{c\{\Gamma_{\mathrm{irr}}\}} , \quad (6.15)$$

that is, $\hat{R}(t) = e^{itH_s^{\times}} R(t)\, e^{-itH_s^{\times}}$ is the derivative $(d/dt)_{\rightarrow}$ of the sum over all connected graphs, on the irreducible components of which are built (ordinary) cumulants. Returning to labeled "unweighted" graphs, we have

$$\hat{R}(t) = (1/i)\left(\frac{d}{dt}\right)_{\rightarrow} \sum_{k=1}^{\infty}\left(\frac{n^k}{k!}\right)$$

$$\times\, {}_{\infty}\langle \mathcal{V}^k \textstyle\sum \Gamma_{\mathrm{conn}}(s, 1, \ldots, k)\rangle_{c\{\Gamma_{\mathrm{irr}}\}} \quad (6.16)$$

$$= (n/i)\, {}_{\infty}\langle \mathring{f}_{s1}\rangle + \frac{n^2}{2i}\left[\left(\frac{d}{dt}\right)\right.$$

$$\times\, {}_{\infty}\langle \mathcal{V}^2 (2 f_{s1} f_{12} + f_{s1} f_{s2} f_{12} + f_{s1} f_{s2})\rangle$$

$$\left. -2\, {}_{\infty}\langle \mathcal{V} f_{s1}\rangle\, {}_{\infty}\langle \mathcal{V} \dot{f}_{s2}\rangle\right] + \cdots . \quad (6.17)$$

One may return to the noninteraction representation by first writing each quantity $\langle \prod_{\mu<\nu}^{(\Gamma)} f_{\mu\nu}\rangle$ as the average of a sum of e-bonded graphs $\gamma = \prod_{\mu<\nu}^{(\gamma)} e_{\mu\nu}$, where $e_{\mu\nu} = f_{\mu\nu} + 1 = \exp[i\int_{-i\beta}^{\tau} dz\, W_{\mu\nu}(z)]$:

$$\langle \Gamma\rangle = \langle \textstyle\sum^{(\Gamma)} \gamma\rangle .$$

Now,

$$\langle \gamma\rangle = Z_1^{-k} e^{\beta H_s} (\mathrm{Tr}_B\, e^{-\beta H^{\gamma}} e^{itH^{\gamma\times}})\, e^{-itH_s^{\times}} ,$$

where $Z_1 \equiv \mathrm{Tr}_1 e^{-\beta H_1}$, k is the number of perturbers in the graph γ, and

$$H^{\gamma} = H_s + \textstyle\sum H_j + \sum_{\mu<\nu}^{(\gamma)} V_{\mu\nu} ,$$

$\sum H_j$ being the sum of the Hamiltonians of the k perturbers in γ, and the sum $\sum_{\mu<\nu}^{(\gamma)}$ is over the e bonds in the graph γ. Note that the graphs γ can be of any type, and $\langle \mathcal{V}^k \gamma\rangle$ may diverge in the limit $\mathcal{V} \to \infty$; it is only the sum $\langle \mathcal{V}^k \sum^{(\Gamma)} \gamma\rangle$, where Γ is connected, which has a proper limit.

VII. DISCUSSION OF DENSITY EXPANSION

In order to discuss the physical significance of the various quantities entering the density expansion, it is convenient to express the quantum-mechanical quantities in a form which provides and can be analyzed with reference to a classical image of the gas; this can be achieved by use of Feynman's path-integral formulation of quantum mechanics, or more simply by the use of small wave packets which follow approximately classical trajectories. The latter method is less rigorous and of less general applicability than the path-integral method, but it suffices for the qualitative discussion we want to give.

The products of Liouville operators $f_{\mu\nu}$ in our expressions operate on $\prod_j I_j D$, where I_j is the unit operator in the space of perturber j, and D is the radiator dipole moment operator. We can write

$$I_j = \textstyle\sum_n \int d^3 r_j\, d^3 k_j\, |r_j, k_j; n\rangle\langle r_j, k_j; n| ,$$

where $|r_j, k_j; n\rangle$ is a minimum uncertainty Gaussian wave packet[17] centered at (r_j, k_j) in the phase space of perturber j (r is the spatial coordinate and k the momentum), and n labels the internal states of the atom; the unit operator in the space of the translational motion of the radiator is also written in that form. In order to keep the discussion simple, we assume that the atoms do not undergo collision-induced electronic transitions (adiabatic assumption), so that a single-particle wave-packet product $e^{itH}\prod_j |r_j, k_j, n_j\rangle$ follows a unique trajectory in phase space and does not become, under the effect of collisions, a superposition of packets with different internal states which may follow different trajectories (since the internal states of the atoms affect the dynamics of collisions). Because both $|\ \rangle$ and $\langle\ |$ in the Liouville wave packet $|r_j, k_j, n_j; t\rangle\langle r_j, k_j, n_j; t|$ follow the same unique trajectory, we can speak of the trajectory followed by the Liouville wave packet. Allowing for the possibility of collision-induced transitions introduces interference effects between different "paths," arising from the cross terms in $|\ \rangle\langle\ |$ if each of $|\ \rangle$ and $\langle\ |$ is a superposition of states, but does not alter the basic discussion.

The discussion given in this section is not intended to be rigorous; its purpose is to indicate the physical significance of the various quantities entering the density expansion of $R(t)$, and to reveal the physical structure of $R(t)$. We neglect the possibility of bound-state formation between the radiator and perturbers.

A. Significance of $f_{\mu\nu}$-Binary Collisions

Let $\psi = \phi_\mu \phi_\nu$ be a product of two single-particle wave packets, depending, respectively, on the coordinates of particles μ and ν, and let us consider $\dot{f}_{\mu\nu}(t)$ operating on the Liouville state $|\psi\rangle\langle\psi|$:

$$\dot{f}_{\mu\nu}(t)|\psi\rangle\langle\psi| = iT_{\rightarrow} \exp[i \textstyle\int_{-i\beta}^{t} dz\, W_{\mu\nu}(z)]$$

$$\times (V_{\mu\nu}(t)|\psi\rangle\langle\psi| - |\psi\rangle\langle\psi| V_{\mu\nu}(t))\,; \qquad (7.1)$$

for this expression not to vanish, the two particles must be interacting, that is, the packets $|\psi_\mu(t)\rangle = e^{-itH_\mu}|\psi_\mu\rangle$ and $|\psi_\nu(t)\rangle$ must be colliding at time t. In order to separate the intrinsic time behavior from the "free" time evolution, we perform a time translation which brings the last interaction $V_{\mu\nu}(t)^{\times}$ to time zero, and define

$$m_{\mu\nu}^{t} \equiv (1/i)\, e^{-itH_0^{\times}} \dot{f}_{\mu\nu}(t) e^{itH_0^{\times}}$$

$$= T_{\rightarrow} \exp[i \textstyle\int_{-i\beta-t}^{0} dz\, W_{\mu\nu}(z)]\, V_{\mu\nu}^{\times}\,, \qquad (7.2)$$

where the integral $\int_{-i\beta-t}^{0} dz$ is along the contour of Fig. 1 displaced by t to the left, and with $\tau = t$.

Since the collisions last only for a finite time t_c, the collision duration, only the interactions $W_{\mu\nu}(z)$ with $\mathrm{Re}\, z > -t_c$ are nonvanishing, since the collision must end at or after time zero for $V_{\mu\nu}^{\times}$ not to vanish. Thus when t is increased beyond t_c, nothing is added to the phase $\int_{-i\beta-t}^{0} dz\, W_{\mu\nu}(z)$, that is, $m_{\mu\nu}^{t}$ becomes independent of time and equal to $m_{\mu\nu}^{\infty}$:

$$m_{\mu\nu}^{t} \xrightarrow{t > t_c} m_{\mu\nu}^{\infty} = T_{\rightarrow} \exp[i \textstyle\int_{-\infty}^{0} dt\, V(t)^{\times}]\, V^{\times}\,. \qquad (7.3)$$

We note that the imaginary-time interactions do not appear in $m_{\mu\nu}^{\infty}$; that is, if the collision of particles μ and ν occurs a sufficiently long time after the "initial" time, then they cannot be correlated at that initial time since they are far apart from each other, and the density matrix is a product of one-particle matrices, so that the interaction representation density matrix $e^{\beta(H_\mu + H_\nu)}\, e^{-\beta(H_\mu + H_\nu + V_{\mu\nu})}$ becomes unity. The operator $m_{\mu\nu}^{\infty}$ has the structure of a T matrix, and it may be called a Liouville-space T matrix for the scattering of particles μ and ν. Note that provided it is not entangled with other operators by the time-ordering operation included in $\langle\;\rangle$,

$$m_{\mu\nu}^{\infty} = \lim_{t\to\infty} e^{-itH_0^{\times}} e^{it(H_0 + V_{\mu\nu})^{\times}} V_{\mu\nu}^{\times}\,, \qquad (7.4)$$

which is a more familiar form for defining a T matrix.

B. Operator $R(t)$ to First Order in the Density

The expression of $R(t)$ to first order in the density, designated $R^{(1)}(t)$, is given, according to (6.16), by

$$\hat{R}^{(1)}(t) = (n/i)_{\infty} \langle \mathcal{V} \dot{f}_{s1}(t) \rangle$$

$$= n e^{itH_s^{\times}}\, {}_{\infty}\langle \mathcal{V}\, m_{s1}^{t} \rangle e^{-itH_s^{\times}}\,,$$

that is,

$$R^{(1)}(t) = n\, {}_{\infty}\langle \mathcal{V}\, m_{s1}^{t} \rangle$$

$$= n \lim (\mathcal{V}/Z_1)\, \mathrm{Tr}_1\, e^{-\beta H_1} [e^{-itH_0^{s1}} e^{\beta H_0^{s1}} e^{-\beta H^{s1}} e^{itH_0^{s1}}]$$

$$\times e^{-itH_0^{s1\times}} e^{itH^{s1\times}}\, V_{s1}^{\times}\,, \qquad (7.5)$$

where H_μ is the Hamiltonian of the μth particle, $H_0^{\mu\nu} \equiv H_\mu + H_\nu$, $H^{\mu\nu} \equiv H_\mu + H_\nu + V_{\mu\nu}$, $Z_1 \equiv \mathrm{Tr}_1 e^{-\beta H_1}$, and Tr_1 is the trace over the coordinates of perturber 1; note that Z_1 is proportional to $\mathcal{V}$, so that $\lim(\mathcal{V}/Z_1)$ as $\mathcal{V} \to \infty$ is well defined.

According to (7.3), the asymptotic limit of $R^{(1)}(t)$ is (excluding bound states)

$$R^{(1)}(\infty) = n(\mathcal{V}/Z_1)\, \mathrm{Tr}_1\, e^{-\beta H_1} m_{s1}^{\infty}\,; \qquad (7.6)$$

this is, the result first obtained by Baranger[7] and then rederived by Fano,[5] both assuming from the start a zero-correlation initial-density matrix. It is seen that the initial correlations do not affect $R^{(1)}(\infty)$, and $R(\infty)$ in general, which determines the impact part of the spectrum; but they do affect $R(t)$ at small times [and also the bound-state part of $R(t)$], and consequently the initial correlations affect the wings of the spectrum (and the bound-state spectrum), as discussed in Sec. IX.

C. Irreducible Graphs

Any graph $\Gamma = \prod_{\mu<\nu}^{(\Gamma)} f_{\mu\nu}$ can be written in the form

$$\Gamma = \prod_{\mu<\nu}^{(\Gamma)} [\textstyle\int_{-i\beta}^{\tau} dz_{\mu\nu}\, \dot{f}_{\mu\nu}(z_{\mu\nu})]$$

$$= \prod_{\mu<\nu}^{(\Gamma)} [i \textstyle\int_{-i\beta}^{\tau} dz_{\mu\nu}\, m_{\mu\nu}^{z_{\mu\nu}}(z_{\mu\nu})]\,, \qquad (7.7)$$

where

$$m_{\mu\nu}^{z}(z') \equiv (1/i)\, e^{i(z'-z)H_0^{\times}} \dot{f}_{\mu\nu}(z) e^{-i(z'-z)H_0^{\times}}\,,$$

and the product $\prod_{\mu<\nu}^{(\Gamma)}$ is over the particle pairs connected by a bond in the graph Γ. It is argued in Appendix D that if Γ is irreducible, then $\langle \prod_{\mu<\nu}^{(\Gamma)} \dot{f}_{\mu\nu}(z_{\mu\nu}) \rangle$ vanishes unless all the collision times $\mathrm{Re}\, z_{\mu\nu}$ are clustered together; thus, an irreducible graph corresponds to a collision of the radiator with a *cluster* of perturbers, which may be called an elementary system-bath interaction. Let us call t_Γ the maximum duration of such a collision, and consider

$$\langle m_\Gamma^t \rangle \equiv (1/i)\,\langle e^{-itH_0^\times}\dot{\Gamma}(t)e^{itH_0^\times}\rangle$$
$$= \sum_{\mu<\nu}^{(\Gamma)} \Big\langle \prod_{\substack{\alpha<\beta \\ (\alpha,\beta)\neq(\mu,\nu)}}^{(\Gamma)} \Big[i\int_{-i\beta-t}^{0} dz_{\alpha\beta} \times m_{\alpha\beta}^{z_{\alpha\beta}+t}(z_{\alpha\beta})\Big]\, m_{\mu\nu}^t(0)\Big\rangle\,; \qquad (7.8)$$

because of the factors $m_{\mu\nu}^t(0)$, only collisions occuring around time zero contribute to (7.8), and we see that as t increases beyond t_Γ, nothing is added to the integrals; thus, when $t \gg t_\Gamma$, $\langle m_\Gamma^t \rangle$ becomes equal to $\langle m_\Gamma^\infty \rangle$, which can be termed the averaged T matrix for the multiple collisions represented by the irreducible graph Γ. We note that $\langle m_\Gamma^\infty \rangle$ is given by (7.8) with the lower integration limits replaced by $-\infty$, and each $m_{\alpha\beta}^{z'+t}(z')$ replaced by $m_{\alpha\beta}^\infty(z')$; again, the initial correlations disappear in the large time limit, since then the "initial time" occurs long before the collision, so that the radiator and the perturbers involved are far from each other and uncorrelated at that initial time.

D. Density Expansion of $B(\tau)$

According to (6.12), we can write $B(\tau)$ in the form

$$B(\tau) = \langle \exp[\textstyle\int_{-i\beta}^{\tau} dz \sum' \dot{\Gamma}'_{\rm irr}(z)]\rangle\ , \qquad (7.9)$$

which is analogous in form to expression (4.6), with $W = \sum_{\mu<\nu} W_{\mu\nu}$ replaced by $(1/i)\sum'\dot{\Gamma}'_{\rm irr}$; this correspondence between $\dot{\Gamma}'_{\rm irr}$ and $V_{\mu\nu}$ emphasizes the role of $\dot{\Gamma}'_{\rm irr}$ as an "elementary" system-bath interaction. Expanding (7.9), we have

$$B(\tau) = \sum_{k=0}^{\infty} (1/k!) \sum_{j_1}{}' \sum_{j_2}{}' \cdots \sum_{j_k}{}' \int_{-i\beta}^{\tau} dz_1 \int_{-i\beta}^{\tau} dz_2 \cdots \times \int_{-i\beta}^{\tau} dz_k \langle \dot{\Gamma}'_{j_1}(z_1)\dot{\Gamma}'_{j_2}(z_2)\cdots\dot{\Gamma}'_{j_k}(z_k)\rangle\ , \qquad (7.10)$$

where $\sum_j' \dot{\Gamma}_j'$ denotes the sum over all irreducible graphs; each $\dot{\Gamma}_j'$ represents a collision of the radiator with the bath, and $\langle \prod_{i=1}^k \dot{\Gamma}'_{j_i}(z_i)\rangle$ represents a succession of k collisions; these are integrated over all possible sets of collision times, then summed over all possible sets of k collisions, and finally summed over k: $B(\tau)$ thus represents the sum over all possible histories of the radiator in the time interval $-i\beta$ to τ. As is well known, the expansion of $B(\tau)$ in powers of V has a similar interpretation, which can be visualized in terms of Feynman diagrams; but the expansion (7.10) has a more immediate physical meaning, for its "elementary" interactions represent actual physical processes, unlike the "interactions" $V(t)$ which are a concept introduced precisely to allow interpreting the perturbation expansion as a sum over histories, but do not represent actual physical processes.

E. Density Expansion of $R(t)$

In order to see the physical significance of the successive terms in the density expansion $R = \sum_k R^{(k)}$, we first consider the case of very low densities, at which (almost) only binary collisions occur, and then consider the corrections corresponding to multiple collisions that must be made as the density is increased. In the binary-collision limit, only the binary irreducible graphs $\dot{f}_{sj}$ are retained, and since the collisions are well separated and therefore time deentangled, we have $\langle \Pi_j \dot{f}_{sj}(z_j)\rangle\rangle = \Pi_j \langle \dot{f}_{sj}(z_j)\rangle$, so that

$$B(\tau) = \sum_{k=0}^{\infty} (1/k!) \int_{-i\beta}^{\tau} dz_1 \cdots \int_{-i\beta}^{\tau} dz_k \times T_{z\to}\langle \dot{f}_{s1}(z_1)\rangle \cdots \langle \dot{f}_{sk}(z_k)\rangle$$
$$= T_{z\to}\exp[\textstyle\int_{-i\beta}^{\tau} dz\, \langle \dot{f}_{s1}(z)\rangle]\ ; \qquad (7.11)$$

comparing with (7.5), it is seen that the first-order term in the density expansion of $R(t)$ represents the effect of *mutually independent* binary collisions.

If now the possibility of triple collisions is included, the sum over all histories must include that possibility in addition to binary collisions. The sum (7.11) does include the possibility of overlapping binary collisions, but it treats them as independent; thus, for each triple collision in a particular history of the radiator, a correction

$$\langle \dot{f}_{si}\dot{f}_{ij} + \dot{f}_{sj}\dot{f}_{ij} + \dot{f}_{si}\dot{f}_{sj}\dot{f}_{ij}\rangle + (\langle \dot{f}_{si}\dot{f}_{sj}\rangle - T_\to\langle \dot{f}_{si}\rangle\langle \dot{f}_{sj}\rangle)$$

must be added to the independent collision factor $T_\to\langle \dot{f}_{si}\rangle\langle \dot{f}_{sj}\rangle$, the second term representing the effect of time entanglement, and the first term the effect of possible interactions between the two perturbers. The sum of (7.11) plus all these corrections can be seen to be what the expansion of $T_\to \exp[i\int_{-i\beta}^{\tau} dz\,(\hat{R}^{(1)} + \hat{R}^{(2)})]$ yields.

Similarly, the higher-order terms in the density expansion of R represent corrections arising from multiple collisions of corresponding order. Thus, $\langle \prod_j^{(\Gamma)} \dot{\Gamma}_{{\rm irr}_j}(z_j)\rangle_{c\{\Gamma_{\rm irr}\}\to}$ is a correction corresponding to the overlap and time entanglement of the collisions $\dot{\Gamma}_{{\rm irr}j}$, and it vanishes if they do not actually overlap, i.e., if the times ${\rm Re}\,z_j$ are not clustered, for this case is already accounted for in terms of lower order in the density. We can define, in analogy with (7.2) and (7.8),

$$i\langle m_\Gamma^t\rangle_c \equiv \langle e^{-itH_0^\times}\dot{\Gamma}(t)\,e^{itH_0^\times}\rangle_{c\{\Gamma_{\rm irr}\}\to}\ , \qquad (7.12)$$

which has an expression similar to (7.8), but with the $m_{\mu\nu}$'s replaced by $m_{\Gamma_{\rm irr}}$'s, and $\langle\ \rangle$ by $\langle\ \rangle_{c\{\Gamma_{\rm irr}\}\to}$. The limit $\langle m_\Gamma^\infty\rangle_c$ may be called the connected averaged T matrix for the multiple collision $\mathbf{\Gamma}$, composed of several overlapping $\dot{\Gamma}_{\mathrm{irr}}$ collisions. We note that it would not be possible to define a T matrix with only the ordinary average $\langle\ \rangle$ of $\dot{\Gamma}$, for then nothing forces the different collisions to overlap in time, and no definite limit would be reached at large times.

The expression of $R(t)$, given by (6.15) and (6.16) can be written

$$R(t)=\sum \langle m^{t}_{\Gamma'_{\mathrm{conn}}} \rangle_{c\{\Gamma_{\mathrm{irr}}\}\rightarrow} \;, \tag{7.13}$$

and in the limit $t\rightarrow\infty$,

$$\begin{aligned} R(\infty) &=\sum \langle m^{\infty}_{\Gamma'_{\mathrm{conn}}} \rangle_{c\{\Gamma_{\mathrm{irr}}\}\rightarrow} \\ &= \langle \exp[i \textstyle\int_{-\infty}^{0} dt \sum' m^{\infty}_{\Gamma'_{\mathrm{irr}}}(t)] \sum' m^{\infty}_{\Gamma'_{\mathrm{irr}}} \rangle_{c\,\{m_{\Gamma_{\mathrm{irr}}}\}\rightarrow} \;, \end{aligned} \tag{7.14}$$

where

$$m^{t}_{\Gamma}(t')=e^{it'H_0^{\times}} m^{t}_{\Gamma}\, e^{-it'H_0^{\times}} \;.$$

The structural similarity between expressions (7.14), (5.4), and (7.3) suggests calling $R(\infty)$ a connected averaged T matrix for the interaction of the system with the bath. Note that the initial correlations do not appear in $R(\infty)$.

In the above discussion, it was assumed that no bound states are formed between the radiator and perturbers; the effect of bound states is not difficult to assess in the first-order term $R^{(1)}(t)$, to which they add terms oscillating forever, but their effect in the higher-order terms is very complicated. We note that if we choose $V=V_{sB}$ and $H_0=H_s+H_B^{(T)}=H_s+H_B+V_B$, we can obtain an expansion similar to (6.14)–(6.16), but with only irreducible graphs of one perturber; each term in this expansion still depends on the density through $H_B^{(T)}$. Such an expansion seems better suited to treat the effect of radiator-perturber bound states, but this will not be discussed here.

VIII. TRANSLATIONAL MOTION OF RADIATOR

The time-evolution operator $U(\tau)$ operates in the space of the radiator, which includes its translational and internal coordinates; since the dipole moment operator D pertains only to the internal motion of the radiator, we can immediately perform the average over the translational, or center-of-mass (c.m.), coordinates. We have

$$H_s=K_s+H_e \;, \tag{8.1}$$

where K_s is the c.m. kinetic energy operator, and H_e the Hamiltonian for the internal, or electronic, motion of the radiator. We can then write Eq. (2.6) in the form

$$I(\tau)=\mathrm{Tr}_e D\rho_e B_e(\tau)e^{i\tau H_e^{\times}}D \;, \tag{8.2}$$

$$B_e(\tau)={}_{\mathrm{c.m.}}\langle B(\tau)\rangle \;, \tag{8.3}$$

where

$${}_{\mathrm{c.m.}}\langle\!\langle\ \rangle\!\rangle \equiv \mathrm{Tr}_{\mathrm{c.m.}}\,\rho_{\mathrm{c.m.}}(\ ) \;,$$

$$\rho_{\mathrm{c.m.}}\equiv e^{-\beta K_s}/Z_{\mathrm{c.m.}} \;, \quad Z_{\mathrm{c.m.}}\equiv \mathrm{Tr}_{\mathrm{c.m.}}\,e^{-\beta K_s} \;,$$

$$\rho_e\equiv e^{-\beta H_e}/Z_e \;, \qquad Z_e\equiv \mathrm{Tr}_e e^{-\beta H_e} \;.$$

We may substitute for $B(\tau)$ its expression (6.12), and obtain

$$B_e(\tau)=B_e(0)T_{\rightarrow}\exp[i\textstyle\int_0^{\tau} dt\,\hat{R}_e(t)] \;, \tag{8.4}$$

where $\hat{R}_e(t)$ has the same expression (6.15) as $\hat{R}(t)$, but with all the bath averages $\langle\ \rangle$ replaced by the bath and translational average

$${}_{B\mathrm{c.m.}}\langle\ \rangle \equiv {}_{\mathrm{c.m.}}\langle\!\langle\ \rangle\!\rangle = \mathrm{Tr}_{\mathrm{c.m.}}\,\rho_{\mathrm{c.m.}}\,\mathrm{Tr}_B\,\rho_B\,T_{\rightarrow}(\ ) \;;$$

effectively, the translational coordinates of the radiator have been included in the bath, the system of interest consisting of only its internal coordinates. Alternatively, we may consider $R(t)$ as an "interaction" between the internal and translational motions of the radiator, as is suggested by Eqs. (3.1) or (1.1) with

$$L(t)=K_s^{\times}+H_e^{\times}+R(t) \;;$$

with this point of view, we rather substitute expression (5.1) of $B(\tau)$ into (8.3), which yields

$$\hat{R}_e(t)={}_{\mathrm{c.m.}}\langle \exp[i\textstyle\int_{-i\beta}^{t} dz\,\hat{R}(z)]\,\hat{R}(t)\rangle_{c\{R\}\rightarrow} \;, \tag{8.5}$$

where the cumulants ${}_{\mathrm{c.m.}}\langle\ \rangle_{c\{R\}\rightarrow}$ are constructed with the interactions R and the average ${}_{\mathrm{c.m.}}\langle\ \rangle$.

We note that the bath-c.m. average ${}_{B\mathrm{c.m.}}\langle\ \rangle$ of a product of irreducible graphs, representing collisions of the radiator with different clusters of perturbers, does not in general factorize when the collisions do not overlap in time: This is because each irreducible graph depends on the c.m. coordinates of the radiator, and furthermore, even if successive collisions are separated by a large time, they can be correlated, for the perturber velocity distritribution seen by the radiator depends on its own velocity and thus on its last collision (the velocity distribution of the perturbers is isotropic in the laboratory frame of reference, and therefore anisotropic in the frame of the moving radiator). This intercollision correlation causes an observable effect in collision-induced spectra[18]; their effect on ordinary spectra is much smaller and probably negligible in general.

The correlation function $I(\tau)$ is given by

$$I(\tau)=\mathrm{Tr}_e D\sigma_e U_e(\tau)D \;,$$

where

$$\sigma_e\equiv \mathrm{Tr}_{\mathrm{c.m.}}\,\mathrm{Tr}_B\rho \;,$$

$$U_e(\tau)=\sigma_e^{-1}\,\mathrm{Tr}_{\mathrm{c.m.}}\,\mathrm{Tr}_B\,\rho e^{i\tau H^{\times}}=B_e(0)^{-1}B_e(\tau)e^{i\tau H_e^{\times}} \;;$$

we have again for $U_e(\tau)$ the expression (3.6), but with R replaced by R_e everywhere.

IX. SPECTRUM TO FIRST ORDER IN DENSITY

To first order in the perturbing-gas density, the time-evolution operator $U_e(\tau)$ is given by [cf. Eqs. (3.5)–(3.8) with R replaced by R_e]

$$U_e^{(1)}(\tau) = A_e^{(1)} e^{i\tau\mathcal{L}_e^{(1)}} - i\int_\tau^\infty dt\, e^{itH_e^\times} \tilde{R}_e^{(1)}(t) e^{-itH_e^\times} e^{i\tau H_e^\times} , \qquad (9.1)$$

where the superscript (1) indicates quantities calculated to first order in the density, and the subscript e means that R is replaced by R_e everywhere. The second term in (9.1) is

$$-(A_e^{(1)} - 1)e^{i\tau H_e^\times} + i\int_0^\tau dt\, e^{itH_e^\times} \tilde{R}_e^{(1)}(t)\, e^{i(\tau-t)H_e^\times}$$
$$= J(\tau) - [A_e^{(1)} - 1 + J(0)]\, e^{i\tau H_e^\times} - i\int_0^\tau dt\, e^{itH_e^\times} \overline{R}_e^{(1)}\, e^{i(\tau-t)H_e^\times} ,$$

where

$$J(\tau) \equiv n_{B\,\mathrm{c.m.}} \langle f_{s1}(\tau) + 1 \rangle e^{i\tau H_e^\times}$$
$$= n(1/Z_{\mathrm{c.m.}} Z_1)\, e^{\beta H_e}\, \mathrm{Tr}_{\mathrm{c.m.}} \mathrm{Tr}_j\, e^{-\beta H^{sj}}\, e^{i\tau H^{sj\times}} \qquad (9.2)$$

is the time-evolution operator in the presence of only one perturber; the Fourier transform of $J(\tau)$ defines the one-perturber spectrum

$$I_{\text{one-pert}}(\omega) = \mathrm{Tr}_e D\rho_e J(\omega) D . \qquad (9.3)$$

Thus, to first order in the density, the spectrum is

$$I(\omega) = I_{\mathrm{imp}}(\omega) + I_{\text{one-pert}}(\omega) + K(\omega) , \qquad (9.4)$$

where

$$I_{\mathrm{imp}}(\omega) = \mathrm{Tr}_e D\sigma_e^{(1)} A_e^{(1)} [i(\omega - H_e^\times - \overline{R}_e^{(1)})]^{-1} D$$

is the impact spectrum, and

$$K(\omega) = \mathrm{Tr}_e D\rho_e [i(A_e^{(1)} - 1 + J(0))\,(\omega - H_e^\times - i0)^{-1} + i(\omega - H_e^\times - i0)^{-1} \overline{R}_e^{(1)} (\omega - H_e^\times - i0)^{-1}] D .$$

The spectrum equals the sum of the impact and one-perturber distributions, plus a correction $K(\omega)$ which diverges at the resonance frequencies (the eigenfrequencies of $H_e^\times$). We note that the sum $I_{\text{one-pert}}(\omega) + K(\omega)$ is regular at the resonance frequencies, since its Fourier transform, the second term in (9.1), vanishes at large values of τ; thus, the role of $K(\omega)$ near the resonance frequencies is to cancel out the singularities exhibited by the one-perturber spectrum. In the wings, the role of $K(\omega)$ is to cancel the wings of the impact spectrum $\mathrm{Re} I_{\mathrm{imp}}(\omega)$; indeed, one sees readily that to first order in the density, $\mathrm{Re} I_{\mathrm{imp}}(\omega)$ and $-\mathrm{Re} K(\omega)$ are equal when the frequency ω is such that $|(\omega - H_e^\times)^{-1} \overline{R}_e^{(1)}| \ll 1$, so that at those frequencies, the spectrum is given by the one-perturber distribution [note that we only need consider the real parts, since the power radiated is $(4\omega^4/3c^3) \times \pi^{-1} \mathrm{Re} I(\omega)$].

We notice that the one-perturber spectrum depends on the initial correlation between the radiator and the perturber through the density matrix $e^{-\beta H^{sj}} = e^{-\beta(H_s + H_j + V_{sj})}$ contained in expression (9.2). The effect of this initial correlation is most easily seen by referring to the quasistatic (or statistical) approximation to the line shape[19]; according to that approximation, the intensity radiated at a given frequency is proportional to the relative probability for the atoms to be in configurations which, if frozen, would cause the radiator to radiate at that frequency. This probability depends on the interatomic potential through the Boltzmann factor. Neglecting initial correlations, that is, neglecting V_{sj} in $e^{-\beta H^{sj}}$, results in replacing the Boltzmann factor by unity in the quasistatic spectrum. This can significantly affect the spectrum, especially in the far violet wings which usually result from close-packed configurations, the probability for which is greatly exaggerated if one neglects the Boltzmann factor whose role is to discriminate against those large potential-energy configurations.

X. CONCLUSION

Our treatment centered around the time-evolution operator $U(t)$ which governs the motion of the radiator under the influence of the bath. Though $U(t)$ possesses perturbation expansions, these do not converge uniformally with respect to t, and cannot serve as approximation schemes; $U(t)$ must therefore be expressed in terms of other quantities which have perturbation expansions that *can* be truncated. There are several possibilities, and we have mentioned two, relating to our operators $R(t)$ and $C(\omega)$, respectively. These two operators are different from each other, and treating either of them to a given order in some parameter, such as the (reduced) density, does not constitute identical approximations, but yields different expressions for the spectrum. For instance, it will be argued in a forthcoming paper that by treating $C(\omega)$ to first order in the density, one effectively neglects the effect of multiple collisions, whereas we saw that the same approximation on $R(t)$ is equivalent to treating all radiator-perturber collisions as *independent* from each other (though possibly overlapping in time). This is strictly correct in the binary collision (low-density) limit, but it may also constitute a reasonably good approximation at higher densities where multiple collisions occur with a non-negligible frequency; that this may be the case is well known in the adiabatic theory of pressure broadening,[20] where this independent-collision approximation allows us to understand such experimental features as the pressure shift of the wing structure (e.g., satellites), and other fine structure in the wings which arise from simultaneous collisions of the radiator with more than one perturber.[20]

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APPENDIX A: CUMULANT EXPANSIONS

1. Preliminary Considerations

When one expects a *function* $G(\tau)$ to behave (perhaps only asymptotically) as the exponential of a simpler or more accessible function, it is appropriate to concentrate one's attention directly on

$$\ln G=\ln[1+(G-1)]\equiv -\sum_{n=1}^{\infty}(1-G)^n/n \ . \tag{A1}$$

If $G(\tau)$ is an *operator*, $\ln G$ as defined by (A1) still satisfies $G=e^{\ln G}$; but in this case, one would expect $G(\tau)$ to be given by the *time-ordered* exponential of some operator $F(t)$ rather than by an ordinary exponential $e^{A(\tau)}$, which is rarely or never met in physical problems [unless $A(\tau)=\tau B$, where B is independent of τ], for the reason probably that the derivative of such a function is extremely complicated if $A(t)$ and $\dot{A}(t)\equiv dA/dt$ do not commute (since, e.g., $dA^3/dt=A^2\dot{A}+A\dot{A}A+\dot{A}A^2$). It then seems appropriate to write $G(\tau)$ in the form $T\exp[\int^{\tau} dt\, F(t)]$, where T is a time-ordering operator, and to concentrate one's attention on $F(t)$.

Writing then

$$\begin{aligned} G(\tau)&=G(0)\, T_{\rightarrow}\exp\Big[\int_0^{\tau} dt\, F_{\rightarrow}(t)\Big] \\ &= T_{\leftarrow}\exp\Big[\int_0^{\tau} dt\, F_{\leftarrow}(t)\Big]\, G(0)\ , \end{aligned} \tag{A2}$$

we deduce from the equivalent equations

$$\frac{d}{dt}G(t)=\dot{G}(t)=G(t)F_{\rightarrow}(t)=F_{\leftarrow}(t)G(t) \tag{A3}$$

that

$$F_{\rightarrow}(t)=G(t)^{-1}\dot{G}(t)\ , \quad F_{\leftarrow}(t)=\dot{G}(t)G(t)^{-1}\ ; \tag{A4}$$

here $T_{\rightarrow}$ ($T_{\leftarrow}$) orders operators such that their time arguments increase from left to right (right to left). Note that we require the existence of $G(t)^{-1}$, or $\det G\neq 0$; the equivalent condition $g(t)\neq 0$ is required in order to define the logarithm of a *scalar* function g. In this latter case, an expression similar to (A2)–(A4) is obtained by writing

$$\begin{aligned} g(\tau)=e^{\ln g(\tau)}&=\exp\Big(\ln g(0)+\int_0^{\tau} dt\,\frac{d}{dt}\ln g(t)\Big) \\ &=g(0)\exp\Big(\int_0^{\tau} dt\, g^{-1}\dot{g}\Big)\ . \end{aligned}$$

Comparing

$$F_{\rightarrow}=[1+(G-1)]^{-1}\dot{G}=\sum_{n=1}^{\infty}(-1)^{n-1}(G-1)^{n-1}\dot{G}$$

with

$$\frac{d}{dt}\ln G=\sum_{n=1}^{\infty}(-1)^{n-1}n^{-1}\frac{d}{dt}(G-1)^n\ ,$$

we notice that we can write

$$F_{\rightarrow}(t)=G(t)^{-1}\dot{G}(t)=\left(\frac{d}{dt}\right)_{\rightarrow}\ln G(t)\ , \tag{A5}$$

where the arrow on $(d/dt)_{\rightarrow}$ means that when operating on a product of operators, the differentiated operators must appear to the right of all other operators in the product; e.g.,

$$\left(\frac{d}{dt}\right)_{\rightarrow} ABC=BC\dot{A}+AC\dot{B}+AB\dot{C}\ .$$

If $G(\tau)$ is of the form $G(\tau)=\langle e^{X(\tau)}\rangle$, where $\langle\ \rangle$ is some linear operation such that $\langle 1\rangle=1$, the terms of the expansion of $\ln G$ or $F_{\rightarrow}$ in powers of $X(\tau)$ have interesting properties and are called *cumulants*.

2. "Ordinary" Cumulants

Let X_i, $i=1, 2, \ldots$, be operators, and $\langle\ \rangle$ an operation such that $\langle\prod_i X_i\rangle$ are also operators and such that $\langle 1\rangle=1$. For definiteness, we may think of the X_i's as stochastic variables, and $\langle\ \rangle$ a statistical average. Let λ_i be arbitrary scalar parameters; the cumulants $\langle X_1X_2\cdots X_k\rangle_c$ are defined by the relation

$$\begin{aligned}\langle e^{\sum_i\lambda_iX_i}\rangle=\exp\Big(\sum_{k=1}^{\infty}\ \sum_{j_1\leq}\sum_{j_2\leq}\cdots\sum_{\leq j_k}\lambda_{j_1}\lambda_{j_2}\cdots \\ \times\lambda_{j_k}\langle X_{j_1}X_{j_2}\cdots X_{j_k}\rangle_c\Big)\ ;\end{aligned} \tag{A6}$$

in other words, $\langle X_{j_1}X_{j_2}\cdots X_{j_k}\rangle_c$ is the coefficient of $\lambda_{j_1}\lambda_{j_2}\cdots\lambda_{j_k}$ in the expansion of $\ln\langle\exp(\sum_i\lambda_iX_i)\rangle$. Equation (A6) is written more compactly as

$$\langle e^{\sum\lambda_iX_i}\rangle=\exp(\langle e^{\sum\lambda_iX_i}-1\rangle_c)\ . \tag{A7}$$

Explicitly, the cumulants are given by

$$\begin{aligned}\langle X_1X_2\cdots X_k\rangle_c=\mathrm{Sym}\sum_{m=1}^{k}(-1)^m(m-1)! \\ \times\sum_{P(m)}\prod_{i=1}^{m}\Big\langle\prod_{j\in J_i}X_j\Big\rangle\ ,\end{aligned} \tag{A8}$$

where the sum $\sum_{P(m)}$ is over all partitions of the set $\{1, 2, \ldots, k\}$ into m subsets J_i, $i=1, 2, \ldots, m$, and Sym denotes symmetrization with respect to the X_i's *and* with respect to different factors $\langle\prod_j X_j\rangle$ in a product. We give a few specific examples:

$$\langle X\rangle_c = \langle X\rangle\ , \quad \langle X^2\rangle_c = \langle X^2\rangle - \langle X\rangle^2\ ,$$

$$\langle X^3\rangle_c = \langle X^3\rangle - \tfrac{3}{2}(\langle X^2\rangle\langle X\rangle + \langle X\rangle\langle X^2\rangle) + 2\langle X\rangle^3\ ,$$

$$\langle X_1X_2\rangle_c = \tfrac{1}{2}(\langle X_1X_2\rangle - \langle X_1\rangle\langle X_2\rangle + \langle X_2X_1\rangle - \langle X_2\rangle\langle X_1\rangle)\ ,$$

$$\langle X_1X_2X_3\rangle_c = \mathrm{Sym}(\langle X_1X_2X_3\rangle - \langle X_1X_2\rangle\langle X_3\rangle - \langle X_1X_3\rangle\langle X_2\rangle - \langle X_1\rangle\langle X_2X_3\rangle + 2\langle X_1\rangle\langle X_2\rangle\langle X_3\rangle)\ . \quad \text{(A9)}$$

We note that the cumulants $\langle X_1X_2\ldots X_k\rangle_c$ are linear in each of their arguments.

The set of operators X_i may be labeled by a continuous parameter rather than by a discreet index. We have for instance

$$\ln\langle\exp[\textstyle\int^\tau dt\, X(t)]\rangle = \sum_{k=1}^{\infty} \int^\tau dt_1 \int^{t_1} dt_2 \cdots \int^{t_{k-1}} dt_k \times\langle X(t_1)X(t_2)\cdots X(t_k)\rangle_c = \langle\exp[\textstyle\int^\tau dt\, X(t)] - 1\rangle_c\ . \quad \text{(A10)}$$

3. $c\rightarrow$ Cumulants

Let now

$$\langle\ \ \rangle \equiv \{T_{\rightarrow}\}_{\mathrm{av}}\ ,$$

where $T_{\rightarrow}$ is the time ordering and $\{\ \ \}_{\mathrm{av}}$ some statistical average. The cumulants $\langle X_{j_k}(t_k)X_{j_{k-1}}(t_{k-1})\cdots X_{j_1}(t_1)\rangle_{c\rightarrow}$ are defined by

$$\langle\exp[\textstyle\int^\tau dt \sum_j \lambda_j(t)X_j(t)]\rangle = T_{t_1\rightarrow}\exp\Big(\int^\tau dt_1\int^{t_1}dt_2\cdots\int^{t_{k-1}}dt_k \times\sum_{j_1\leq}\sum_{j_2\leq}\cdots\sum_{\leq j_k}\lambda_{j_1}(t_1)\cdots\lambda_{j_k}(t_k) \times\langle X_{j_k}(t_k)\cdots X_{j_1}(t_1)\rangle_{c\rightarrow}\Big)\ , \quad \text{(A11)}$$

where $T_{t_1\rightarrow}$ orders the cumulants such that the arguments t_1 increase from left to right. Thus the cumulants $\langle\prod_i X_{j_i}(t_i)\rangle_{c\rightarrow}$ are the coefficients of $\prod_i [dt_i\,\lambda_{j_i}(t_i)]$ in the expansion of $(d/dt)_{\rightarrow}\ln\langle\exp[\int^\tau dt \sum_j \lambda_j(t)X_j(t)]\rangle$. Equation (A11) can be written more compactly, setting $\sum_j\lambda_j(t)X_j(t) = X(t)$:

$$\langle\exp[\textstyle\int^\tau dt\, X(t)]\rangle = T_{t\rightarrow}\exp\{\int^\tau dt\,\langle\exp[\int^t dt' X(t')]X(t)\rangle_{c\rightarrow}\} = T_{c\rightarrow}\exp\{\langle\exp[\int^\tau dt\, X(t)] - 1\rangle_{c\rightarrow}\}\ , \quad \text{(A12)}$$

where $T_{c\rightarrow}$ orders the cumulants such that the *largest* time argument in each increase from left to right.

The $c\rightarrow$ cumulants are related to the ordinary cumulants by means of Eq. (A5):

$$\langle\exp[\textstyle\int^t dt'\, X(t')]X(t)\rangle_{c\rightarrow} = \left(\dfrac{d}{dt}\right)_{\rightarrow}\langle\exp[\int^t dt'\, X(t')] - 1\rangle_c\ . \quad \text{(A13)}$$

From this relation, it is seen that the cumulants $\langle\prod_i X_i(t_i)\rangle_{c\rightarrow}$ have the same explicit expressions as the ordinary cumulants $\langle\prod_i X_i\rangle_c$ with the correspondence $X_i \rightarrow X_i(t_i)$, and the difference that in each product $\prod_i\langle\prod_{j\in J_i}X_j(t_j)\rangle$ of expression (A8), the factor $\langle\prod_j X_j(t_j)\rangle$ containing the *largest* time argument is displaced to the right of all other factors. A few specific examples are [$t_1 > t_2 > t_3$, and we write $X_i(t_i) = X_i$ for short]:

$$\langle X_1X_2\rangle_{c\rightarrow} = \langle X_2X_1\rangle - \langle X_2\rangle\langle X_1\rangle\ ,$$

$$\langle X_3X_2X_1\rangle_{c\rightarrow} = \langle X_3X_2X_1\rangle - \langle X_3X_2\rangle\langle X_1\rangle - \langle X_3\rangle\langle X_2X_1\rangle - \langle X_2\rangle\langle X_3X_1\rangle + \langle X_3\rangle\langle X_2\rangle\langle X_1\rangle + \langle X_2\rangle\langle X_3\rangle\langle X_1\rangle\ . \quad \text{(A14)}$$

The $c\rightarrow$ cumulants seem to have first been introduced by Kubo.[8]

4. "Cluster" Property

The most interesting property of $c\rightarrow$ cumulants, from which they derive their importance, is a kind of "cluster" property, which says that the arguments of a cumulant must be "connected" (or "clustered") for it not to vanish. We first define the notion of connectedness in the sense to be used here.

$\langle\ \ \rangle$ *independence*. Two sets of operators $\{X_i : i\in I\}$ and $\{X_j : j\in J\}$ are said to be $\langle\ \ \rangle$ independent if the $\langle\ \ \rangle$ average of a product of operators from both sets factorizes into the product of the averages $\langle\ \ \rangle$ of the operators from each set; in other words, the sets X_i and X_j are $\langle\ \ \rangle$ independent if for any set $L\subset I\cup J$,

$$\langle\prod_{l\in L}X_l\rangle = \langle\prod_{i\in I\cap L}X_i\rangle\langle\prod_{j\in J\cap L}X_j\rangle\ .$$

If a set of operators cannot be divided into two or more $\langle\ \ \rangle$-independent sets, it is said to be $\langle\ \ \rangle$ *connected*.

The $\langle\ \ \rangle$ independence is an extension of the notion of statistical independence. For instance, for the sets $X_i(t_i)$ and $Y_j(t_j)$ to be $\langle\ \ \rangle$ independent, where $\langle\ \ \rangle \equiv \{T_{\rightarrow}\ \}_{\mathrm{av}}$, the X's and Y's must be statistically independent on the one hand, and also they must not be time entangled, that is, all the time arguments of one set must be smaller than all the time arguments of the other set.

Theorem 1 (*Kubo*[8]). We now have the fundamental theorem: If the X_i's in a cumulant $\langle\prod_i X_i\rangle_{c\rightarrow}$ are not $\langle\ \ \rangle$ connected, that is, if they can be divided into two or more $\langle\ \ \rangle$-independent sets, then the cumulant vanishes.

Proof. Let the two infinite sets of operators $X_i(t)$, $i = 1, 2, \ldots$, and $Y_j(t)$, $j = 1, 2, \ldots$, be statistically independent, and let $\lambda_i(t)$ and $\kappa_j(t)$ be arbitrary scalar functions. Denote

$$X \equiv \int_0^a dt \sum_i \lambda_i(t) X_i(t) ,$$

$$Y \equiv \int_a^\tau dt \sum_j \kappa_j(t) Y_j(t) , \quad \tau > a .$$

We then have

$$\begin{aligned}\langle e^{X+Y} \rangle &= \langle e^X \rangle \langle e^Y \rangle \\ &= [T_{c\rightarrow} \exp(\langle e^X - 1\rangle_{c\rightarrow})][T_{c\rightarrow} \exp(\langle e^Y - 1\rangle_{c\rightarrow})] \\ &= T_{c\rightarrow} \exp(\langle e^X - 1\rangle_{c\rightarrow} + \langle e^Y - 1\rangle_{c\rightarrow}) , \end{aligned} \qquad \text{(A15)}$$

and also

$$\begin{aligned}\langle e^{X+Y} \rangle &= T_{c\rightarrow} \exp(\langle e^{X+Y} - 1\rangle_{c\rightarrow}) \\ &= T_{c\rightarrow} \exp(\langle e^X - 1\rangle_{c\rightarrow} + \langle e^Y - 1\rangle_{c\rightarrow} \\ &\quad + \langle (e^X - 1)(e^Y - 1)\rangle_{c\rightarrow}) . \end{aligned} \qquad \text{(A16)}$$

Equality of (A15) and (A16) implies the vanishing of the term $\langle (e^X - 1)(e^Y - 1)\rangle_{c\rightarrow}$ mixing the two $\langle \ \rangle$-independent sets $X_i(t_i)$, $t_i < a$ and $Y_j(t_j)$, $t_j > a$; since the functions $\lambda_i(t)$ and $\kappa_j(t)$ can be made arbitrary, this implies in turn the vanishing of all $c\rightarrow$ cumulants containing *both* $X_i(t_i)$'s and $Y_j(t_j)$'s.

Note that the ordinary cumulants do not have the property theorem 1, unless all quantities of the type $\langle \Pi_i X_i \rangle$ commute with each other, in which case, of course, the ordinary and $c\rightarrow$ cumulants are identical.

5. Interpretation

The cumulant expansion may be viewed as an expansion in orders of correlation: Retaining only the cumulants of order $\leq k$ is equivalent, according to theorem 1, to assuming that there are no $\langle \ \rangle$-connected groups of more than k operators $X_i(t_i)$, or that they may be neglected. If, for instance, we assume that $X(t)$ is never correlated with itself at different times, we have

$$\langle \exp[\int^\tau dt\, X(t)] \rangle = 1 + \sum_{k=1}^{\infty} \int^\tau dt_1 \int^{t_1} dt_2 \cdots \int^{t_{k-1}} dt_k \times \langle X(t_k) X(t_{k-1}) \ldots X(t_1) \rangle \qquad \text{(A17)}$$

$$\rightarrow 1 + \sum_{k=1}^{\infty} \int^\tau dt_1 \cdots \int^{t_{k-1}} dt_k \langle X(t_k)\rangle \langle X(t_{k-1})\rangle \cdots \langle X(t_1)\rangle \qquad \text{(A18)}$$

$$= T_\rightarrow \exp[\int^\tau dt \langle X(t)\rangle] = T_\rightarrow \exp[\int^\tau dt\, \langle X(t)\rangle_{c\rightarrow}] , \qquad \text{(A19)}$$

that is, only the first-order cumulant is retained. If one includes the possibility of pairwise correlations between values of $X(t)$ at different times, and adds corrections to (A18) corresponding to each possible combination of pairs of operators, one obtains

$$\langle \exp[\int^\tau dt\, X(t)] \rangle \rightarrow T_\rightarrow \exp[\int^\tau dt \langle X(t)\rangle_{c\rightarrow} + \int^\tau dt \int^t dt' \, \langle X(t') X(t)\rangle_{c\rightarrow}] ,$$

which includes the second-order cumulant. The higher-order cumulants are interpreted similarly.

In physical problems, it often occurs that the operators $X(t_i)$, $i = 1, 2, \ldots,$ are $\langle \ \rangle$ connected only if "clustered" in time; in this case, the property theorem 1 implies the *uniform* (with respect to τ) convergence of the cumulant series. The cumulant expansion can thus be viewed as a perturbation expansion in powers of X, which *can* be truncated, unlike the direct expansion (A17) which is generally *not* uniformly convergent and therefore cannot be truncated.

APPENDIX B: GRAPHS, SOME DEFINITIONS AND PROPERTIES

In this Appendix, some definitions and properties of graphs commonly used in the equilibrium theory of classical fluids[9] are stated and adapted to our particular needs.

1. Labeled Graphs

We shall use graphs of the type shown in Fig. 5, consisting of one white circle, some (or no) black circles labeled by numbers, and one (or no) black line connecting each pair of circles. A graph may be viewed and written as the product of its connected parts. Physically, the white circle represents the radiator, the black circles represent perturbers, and the lines connecting circles indicate interaction between the particles represented.

2. Unlabeled Connected Graphs

From here on, we consider only *connected* graphs of one white circle and some (or no) black circles.

When it is not necessary to know *which* particles are represented by the black circles, the attached labels can be removed, with the understanding that distinct black circles correspond to distinct particles. It is clear that distinct *labeled* graphs may yield identical (i.e., topologically equivalent) unlabeled graphs, as shown for instance in Fig. 6. Let the *symmetry number* $\sigma(\Gamma)$ of a graph Γ be the number of permutations (including the identity) of its black circles which leave the graph unchanged, i.e., do not change the bonds. For instance, the graph of Fig. 6 has symmetry number 2. Clearly then, an unlabeled graph of k black circles corresponds to $k!/\sigma(\Gamma)$ distinct labeled graphs. Thus, when it is *permissible* to remove the labels, we

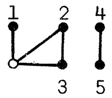

FIG. 5. Example of a labeled graph.

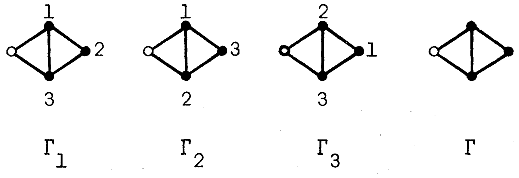

FIG. 6. The distinct labeled graphs Γ_1, Γ_2, and Γ_3 correspond to the same unlabeled graph Γ.

have the relation

$$\sum \Gamma_{\text{conn}}^{k\,(\text{labeled})} = [k!/\sigma(\Gamma_{\text{conn}}^{k})]\Gamma_{\text{conn}}^{k} , \tag{B1}$$

where Γ_{conn}^{k} is an unlabeled connected graph of one white and k black circles, and the sum is over all distinct *labeled* graphs which are topologically equivalent to Γ_{conn}^{k}. We also have

$$\sum_{k=0}^{\infty} (1/k!)\sum \Gamma_{\text{conn}}^{k\,(\text{labeled})} = \sum \Gamma_{\text{conn}}/\sigma(\Gamma_{\text{conn}}) , \tag{B2}$$

where the sum on the right-hand side is over all distinct connected unlabeled graphs of one white and some (or no) black circles.

3. Articulation Circles; 1-Irreducible Graphs

An *articulation circle* in a connected graph is a circle such that its removal separates the graph into two or more disconnected parts. A connected graph which contains no articulation circles is said to be 1 *irreducible;* we have (a) in a 1-irreducible graph, there exist at least two distinct paths connecting each pair of circles; (b) in a 1-irreducible graph, each pair of bonds belongs to at least one closed non-self-intersecting path in the graph.

We shall say that two graphs Γ_1 and Γ_2 are *attached* by their respective black circles i and j, if we simply superpose these two black circles, or equivalently, if we form the product $\Gamma_1\Gamma_2$ and identify the black circles (i.e., the perturbers) i and j. Note that any graph can be constructed by successive attachment of 1-irreducible graphs, the attachment circles being the articulation circles of the given graph.

4. Irreducible Graphs; * Product

If the white circle in a connected graph is not an articulation circle, then we say that the graph is *irreducible.*

We define the * *product* of two connected graphs Γ_1 and Γ_2 [each consisting of one white circle and some (or no) black circles] as the graph $\Gamma_1 * \Gamma_2$ which contains one white circle, and such that upon removing it, the graph separates into two disconnected parts, one of which is Γ_1 minus its white circle, and the other Γ_2 minus its white circle. This type of product is illustrated in Fig. 7. Any connected graph with one white circle can be written as the * product of its irreducible parts.

We can define the * powers of a graph:

$$\Gamma^{*k} \equiv \Gamma * \Gamma * \cdots * \Gamma , \quad k \text{ times};$$

for convenience, the zeroth * power of a graph or of a sum of graphs is defined as the graph consisting of the white circle alone. We can then define the * exponential:

$$\exp_* \Gamma \equiv \sum_{k=0}^{\infty} \Gamma^{*k}/k! .$$

We have the lemma[9]

$$\sum \Gamma_{\text{conn}}/\sigma(\Gamma_{\text{conn}}) = \exp_*[{\textstyle\sum}' \Gamma_{\text{irr}}/\sigma(\Gamma_{\text{irr}})] , \tag{B3}$$

where the sum $\sum \Gamma_{\text{conn}}$ is over all distinct connected graphs of one white and some (or no) black circles, and $\sum' \Gamma_{\text{irr}}$ is the sum over all distinct irreducible graphs of one white and *one or more* black circles (the graph consisting of the white circle alone is excluded in the sum $\sum'$). All graphs here are *unlabeled* graphs.

Proof: Any graph Γ of one white and some (or no) black circles can be written in the form

$$\Gamma = {\textstyle\prod_j'} * (\Gamma_{\text{irr}}^{(j)})^{*p_j} ,$$

where the product $\prod_j'$ is over *all* distinct irreducible graphs of one white and *one or more* black circles (the irreducible graphs not contained in Γ appear with exponent zero). Clearly,

$$\sigma(\Gamma) = {\textstyle\prod_j'} p_j!(\sigma_j)^{p_j} , \quad \sigma_j \equiv \sigma(\Gamma_{\text{irr}}^{(j)})$$

(the σ_j's take account of permutations within each irreducible subgraph, and the p_j!'s correspond to the complete interchange of black circles between identical subgraphs). Thus,

$$\sum \Gamma_{\text{conn}}/\sigma(\Gamma_{\text{conn}}) = \prod_j{}' \sum_{p_j=0}^{\infty} (1/p_j!)(\Gamma_{\text{irr}}^{(j)}/\sigma_j)^{*p_j}$$

$$= \exp_*({\textstyle\sum_j'} \Gamma_{\text{irr}}^{(j)}/\sigma_j) .$$

In our problem, the function represented by the * product of two graphs equals the product of the functions represented by the individual graphs; we can therefore omit the * in (B3), with the understanding that the Γ's stand for the functions represented by the graphs.

APPENDIX C

The following lemma is required for the discussion of Appendix D.

Lemma: Let $H(\{N\})$ be the Hamiltonian for a system of N particles interacting with each other via two-body forces, and let $H(\{N-k\})$ be the Hamiltonian for a subsystem consisting of $N-k$ of the particles. Then $H(\{N-k\})$ commutes with $\text{Tr}^{(k)} f(H\{N\})$, where $f(H\{N\})$ is any function of $H(\{N\})$, and $\text{Tr}^{(k)}$ is the trace over the coordinates of the k other particles:

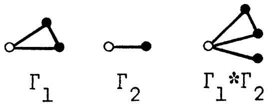

FIG. 7. * product of two graphs.

$$[\mathrm{Tr}^{\{k\}} f(H\{N\}) \,,\; H(\{N-k\})] = 0 \,,$$

or in other words, $\mathrm{Tr}^{\{k\}} f(H\{N\})$ is a function of $H(\{N-k\})$.

Physically, this says in effect that the sum over all possible positions of k particles provides a uniform background which does not affect the motion of the $N-k$ other particles. Specifically, we may think of $H(\{N\})$ as being the Hamiltonian for a group of atoms consisting of a total of N nuclei and electrons, and $H(\{N-k\})$ as corresponding to one atom of one nucleus and $N-k-1$ electrons.

Proof: Let

$$V = \Bigl(\sum_{i\in\{N-k\}}\Bigr)\Bigl(\sum_{j\in\{k\}} V_{ij}\Bigr)$$

be the interaction between the two subgroups of particles, V_{ij} being the interaction between particle i of the $N-k$-particle subgroup, and particle j of the other subgroup; then, $H(\{N\}) = H(\{N-k\}) + H(\{k\}) + V$, where $H(\{k\})$ is the Hamiltonian for the k-particle subgroup. We have

$$\begin{aligned}[\mathrm{Tr}^{\{k\}} f(H\{N\}), H(\{N-k\})] &= \mathrm{Tr}^{\{k\}}[f(H\{N\}), H(\{N-k\})]\\ &= \mathrm{Tr}^{\{k\}}[f(H\{N\}), H(\{N\}) - H(\{k\}) - V]\\ &= -\mathrm{Tr}^{\{k\}}[f(H\{N\}), H(\{k\}) + V] \,.\end{aligned}$$

Now,

$$\begin{aligned}\mathrm{Tr}^{\{k\}}[f(H\{N\}), H(\{k\})] &= \textstyle\sum_n \langle n|\,[f, H(\{k\})]\,|n\rangle\\ &= \textstyle\sum_n (E_n - E_n)\,\langle n|f|n\rangle = 0 \,,\end{aligned}$$

where $|n\rangle$ is a complete set of eigenstates of $H(\{k\})$ of energies E_n. We also have

$$\mathrm{Tr}^{\{k\}}[f, V] = \sum_{i,j} \mathrm{Tr}_j[\mathrm{Tr}^{\{k\}-j} f, V_{ij}] \,,$$

where Tr_j is the trace over the coordinates of particle j, and $\mathrm{Tr}^{\{k\}-j}$ the trace over the $k-1$ other particles in the k-particle subgroup. To complete the proof, we show that $\mathrm{Tr}_j[A, V_{ij}] = 0$ for any operator A. This is obvious since the trace Tr_j can be expanded in terms of a complete set of states of particle j, with particle i as origin [if $\psi_n(r_j)$ is a complete set of states, so is $\psi_n(r_j - r_i)$]; then

$$\mathrm{Tr}_j[A, V_{ij}] = \sum_{m,n} (A_{nm}(V_{ij})_{mn} - (V_{ij})_{mn}A_{nm}) = 0 \,,$$

since

$$(V_{ij})_{mn} = \int dr_j\, \psi_m^*(r_j - r_i) V_{ij}(r_j - r_i)\psi_n(r_j - r_i)$$

is a scalar.

APPENDIX D

We argue in this Appendix that if Γ is an irreducible graph, then $\langle \prod_{\mu<\nu}^{(\Gamma)} \dot f_{\mu\nu}(z_{\mu\nu})\rangle$ is nonvanishing only if the times $\mathrm{Re}(z_{\mu\nu})$ are clustered together. We first consider the case of only two perturbers, which gives a simple illustration of the general arguments used.

1. Two-Perturber Irreducible Graphs

The two-perturber irreducible graphs are $f_{s1}f_{12}$ and $f_{s1}f_{s2}f_{12}$. Let us consider first $\langle \dot f_{s1}(t_1)\dot f_{12}(t_2)\rangle$, which can represent collision processes of the type shown in Fig. 8; clearly, this quantity vanishes if $t_2 > t_1$, for then the last interaction is $V_{12}(t_2)^\times$, and nothing on its right-hand side depends on perturbers 1 or 2, or in fact on any perturber; the last interaction must always involve the radiator for an expression not to vanish: This expresses the fact that the radiator is not influenced by what happens to a perturber *after* it is through interacting with it.

Let now $t_c(s, 1; 2)$ be a time such that if the radiator starts to interact with 1 at some given time, then it will (almost) certainly have ceased interacting with 1 after a time $t_c(s, 1; 2)$ later [we do not take $t_c(s, 1; 2)$ equal to the binary collision duration because of possible recollisions due to the presence of perturber 2 (see below)]. Then, if $t_1 > t_c(s,1;2)$ and $t_2 < t_1 - t_c(s,1;2)$, the operator $\dot f_{12}(t_2)$, in which the *last* interaction occurs at t_2, is time deentangled from $\dot f_{s1}(t_1)$, in which the *first* interaction occurs *later* than time $t_1 - t_c(s, 1; 2)$; we therefore have ($H_0^{12} \equiv H_1 + H_2$, $H^{12} \equiv H_1 + H_2 + V_{12}$, $Z_{12} \equiv \mathrm{Tr}_{12} e^{-\beta H_0^{12}}$):

$$\begin{aligned}Z_{12}\,\langle \dot f_{s1}(t_1)\dot f_{12}(t_2)\rangle &= \mathrm{Tr}_{12} e^{-\beta H_0^{12}}\, T_{\rightarrow} \dot f_{s1}(t_1)\dot f_{12}(t_2)\\ &= \mathrm{Tr}_{12} e^{-\beta H_0^{12}} \dot f_{12}(t_2)\dot f_{s1}(t_1)\\ &= \mathrm{Tr}_{12}\, e^{-\beta H^{12}} e^{it_2 H^{12\times}}(H^{12\times} - H_1^\times - H_2^\times)\, e^{-it_2 H_0^{12\times}} \dot f_{s1}(t_1)\\ &= -\mathrm{Tr}_1[(\mathrm{Tr}_2 e^{-\beta H^{12}})H_1^\times e^{-it_2 H_1^\times} \dot f_{s1}(t_1)] \,;\end{aligned}$$

the operators $H_2^\times$ have vanished since nothing on their right-hand side depends on 2, and $H^{12\times}$ has also disappeared since $\mathrm{Tr}A^\times B = 0$ by the cyclic

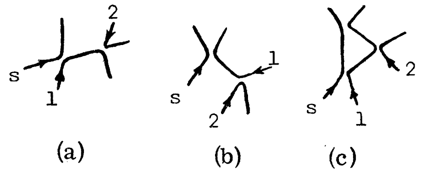

FIG. 8. Possible collision sequences corresponding to $f_{s1}f_{12}$.

property of the trace; now, by the lemma of Appendix C, H_1 commutes with $\mathrm{Tr}_2 e^{-\beta H^{12}}$, so that again by $\mathrm{Tr} A^{\times} B = 0$, the expressions above vanish. This expresses the fact that *on the average*, the radiator is not affected by, or does not "see," the history of a perturber before it starts interacting with it; in other words, the state distribution of a perturber between collisions is always the same (thermal equilibrium). We have thus argued that $\langle \dot{f}_{s1}(t_1) \dot{f}_{12}(t_2) \rangle$ vanishes unless t_2 lies between $t_1 - t_c(s,\ 1;\ 2)$ and t_1.

Recollisions: We mentioned above the possibility of recollisions; indeed, we could have, as shown in Fig. 8(c), two s-1 collisions separated by a 1-2 collision. One can see that the probability for the second s-1 collision to occur a long time after the first is small (note that we are in three dimensions!). To obtain an estimate, we may assume that after its collision with 2, 1 can be heading in any direction and with any velocity within the range defined by the temperature; let us consider a sphere of radius $\bar{v}t$, where $\bar{v}$ is the mean velocity, centered about the region of the first s-1 collision; For the second s-1 collision to occur a time t after the first, 1 must cross the sphere at the same place as s, the probability for which is $\sim t^{-2}$; 1 must also cross the sphere at the same time as s, and the range of velocities allowed for 1 to cross the sphere at a specific time is $\sim t^{-1}$. Hence the probability for the recollision to occur a time t after the first collision is $\sim t^{-3}$. Thus, in general, widely separated recollisions have a small probability, and the interaction between two atoms will always be considered as one collision, even if on finer analysis there are several collisions involved.

Let us now consider $\langle \dot{f}_{s1}(t_1) \dot{f}_{s2}(t_2) \dot{f}_{12}(t_3) \rangle$. If the various collisions are widely separated in time, we have the following possibilities (note that as before, the latest collision must involve the radiator for the expression not to vanish): The 1-2 collision may occur before both the s-1 and s-2 collisions [Fig. 9(a)], or in between these two collisions [Fig. 9(b)]. As for the recollision cycle of Fig. 8(c), and by the same arguments, these three-collision "rings" must be clustered in time to have an appreciable probability. Note that in both cases, the two extreme collisions may be correlated, even if separated by a large time; the latter case represents the simplest example of the reaction of the system on the bath being acted back on the system after a possibly long time.

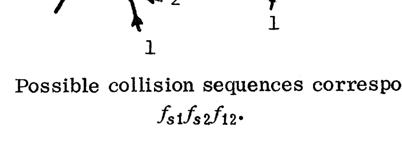

FIG. 9. Possible collision sequences corresponding to $f_{s1} f_{s2} f_{12}$.

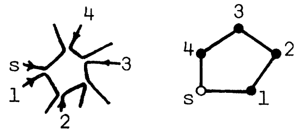

FIG. 10. Example of a collision ring and the corresponding graph.

2. Arbitrary Irreducible Graphs

To argue our proposition in general, we first notice that any irreducible graph can be constructed by starting from some 1-irreducible graph containing the radiator, and then attaching to some of its black circles other 1-irreducible graphs, and then still other 1-irreducible graphs are attached to those, and so on (cf. Appendix B for the definition of 1-irreducible graphs, and the operation of attaching together two graphs). Now, if Υ is a 1-irreducible graph, then $\prod_{\mu<\nu}^{(\Upsilon)} \dot{f}_{\mu\nu}(t_{\mu\nu})$ is clustered in time; this is because any pair of bonds $f_{\mu\nu}$ in a 1-irreducible graph belongs to at least one closed path, or ring, in the graph (cf. Appendix B3), and each "ring" of collisions (e.g., Fig. 10) is clustered in time, by the same type of arguments as used in discussing the three-collision rings of Fig. 9. It then suffices to show that if $\langle \prod_{\mu<\nu}^{(\Gamma)} \dot{f}_{\mu\nu}(t_{\mu\nu}) \rangle$ is clustered in time, where Γ is a connected graph containing the radiator, then $\langle \prod_{\alpha<\beta}^{(\Upsilon)} \dot{f}_{\alpha\beta}(t_{\alpha\beta}) \prod_{\mu<\nu}^{(\Gamma)} \dot{f}_{\mu\nu}(t_{\mu\nu}) \rangle$ is also clustered in time, where Υ is a 1-irreducible graph which does not contain the radiator, and which has one and only one perturber in common with Γ (i.e., Υ is attached to Γ); this will prove the proposition by induction. Since the argument refers mainly to the last interaction times in Υ and in Γ, we consider rather $\langle \dot{\Upsilon}(t_2) \dot{\Gamma}(t_1) \rangle$: Again, t_2 must be smaller than t_1 since the last interaction must involve the radiator. Let $t_c(\Gamma;\ \Upsilon)$ be a time such that if the first interaction in Γ occurs at some given time, then almost certainly, all interactions in Γ (under the possible influence of Υ which may cause recollisions, etc.) will have ceased after a time $t_c(\Gamma;\ \Upsilon)$ later; in other words, $t_c(\Gamma;\ \Upsilon)$ is the duration of the multiple-collision Γ, under the possible influence of the perturbers in Υ.

If now $t_1 > t_c(\Gamma;\ \Upsilon)$ and $t_2 < t_1 - t_c(\Gamma;\ \Upsilon)$, the two graphs $\dot{\Upsilon}(t_2)$ and $\dot{\Gamma}(t_1)$ are time deentangled, and

$$\langle \dot{\Upsilon}(t_2) \dot{\Gamma}(t_1) \rangle = \mathrm{Tr}_B \rho_B \dot{\Upsilon}(t_2) \dot{\Gamma}(t_1) \ .$$

Now, any f-bonded graph $\Upsilon = \prod_{\mu<\nu}^{(\Upsilon)} f_{\mu\nu}$ can be written as a sum of e-bonded graphs $\gamma = \prod_{\mu<\nu}^{(\gamma)} e_{\mu\nu}$, where $e_{\mu\nu} = f_{\mu\nu} + 1 = \exp[i \int_{-i\beta}^{\tau} W_{\mu\nu}(z)\,dz]$, that is, $\Upsilon = \sum^{(\Upsilon)} \gamma$, and

$$\gamma(t) = e^{\beta H_0^{\gamma}} e^{-\beta H^{\gamma}} e^{itH_0^{\gamma\times}} e^{-itH^{\gamma\times}} \ ,$$

where H_0^{γ} is the sum of the Hamiltonians for each perturber in γ, $H_0^{\gamma} \equiv \sum_{i\in\gamma} H_i$, and $H^{\gamma} \equiv H_0^{\gamma} + \sum_{\mu<\nu}^{(\gamma)} V_{\mu\nu}$, the sum $\sum_{\mu<\nu}^{(\gamma)}$ being over the e bonds in γ. We then have $\{Z_{\gamma,\Gamma}=\mathrm{Tr}_{\gamma,\Gamma}\exp[-\beta(H_0^\gamma+H_0^\Gamma)],\ H_0^{\Gamma-j}\equiv H_0^\Gamma-H_j\}$:

$$\mathrm{Tr}_B\rho_B\dot{\Upsilon}(t_2)\dot{\Gamma}(t_1)=\sum{}^{(\Upsilon)}\mathrm{Tr}_B\rho_B\dot{\gamma}(t_2)\dot{\Gamma}(t_1)$$

$$=\sum{}^{(\Upsilon)}Z_{\gamma,\Gamma}^{-1}\,\mathrm{Tr}_{\gamma,\Gamma}\,[e^{-\beta(H_0^\gamma+H_0^{\Gamma-j})}$$

$$\times\, e^{\beta H_0^\gamma}e^{-\beta H^\gamma}e^{it_2H^{\gamma\times}}(H^{\gamma\times}-H_0^{\gamma\times})\,e^{-it_2H_0^{\gamma\times}}\,\dot{\Gamma}(t_1)]$$

$$=-\sum{}^{(\Upsilon)}Z_{\gamma,\Gamma}^{-1}\,\mathrm{Tr}_\Gamma[e^{-\beta H_0^{\Gamma-j}}\,(\mathrm{Tr}_{\gamma-j}e^{-\beta H^\gamma})$$

$$\times\, H_j^\times e^{-it_2H_j^\times}\,\dot{\Gamma}(t_1)]\,,$$

where H_j is the Hamiltonian of perturber j which we take as the perturber common to Υ and Γ, and $\mathrm{Tr}_{\gamma-j}$ is the trace over the perturbers of γ minus perturber j, the trace over which is included in Tr_Γ. Now, by the lemma of Appendix C, H_j commutes with $\mathrm{Tr}_{\gamma-j}e^{-\beta H^\gamma}$, so that the expressions above vanish. Thus the interactions in Υ must overlap in time with those in Γ; this expresses the fact that the graph Γ minus perturber j is not influenced, on the average, by the history of perturber j before interacting with it. This completes the argument to show that if Γ is an irreducible graph, the interactions in $\langle\Gamma\rangle$ are clustered in time; we have excluded the possibility of bound states between the atoms.

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[10] We prefer the form (2.2) to Fano's $\mathrm{Tr}(De^{-i\tau H^\times}\rho D)$ (the two are equal since ρ commutes with H), but the theory can be developed equally well starting with either expressions.

[11] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

[12] In the terminology of Kubo (Ref. 8), $B(\tau)$ would rather be called the *relaxation operator*. Note that if $V_{sB}\rightarrow 0$, $H\rightarrow H_s+H_B+V_B$, so that $Z\rightarrow Z_s\,\mathrm{Tr}_Be^{-\beta(H_B+V_B)}$.

[13] In the adiabatic approximation, $I(\tau)=e^{-ng(\tau)}$ (n is the gas density), and $g(\tau)\rightarrow b-ia+\tau(B-iS)$ at large times [M. Takeo, Phys. Rev. A 1, 1143 (1970)]; $e^{-n(b-ia)}$ corresponds to the operator A. The line shape is, at small ω, given by

$$[(nB)\,\cos(na)+(\omega-nS)\,\sin(na)][(\omega-nS)^2+(nB)^2]^{-1};$$

the constant na affects the shift and width to only second and third order in the gas density, respectively, but it produces an asymmetry of the line with an asymmetry ratio (the ratio of the red-to-violet half-widths) equal to $1-na+\cdots$, which deviates from unity in the first order of density.

[14] We used $T_\rightarrow\exp[\int_a^b dt\,F(t)]T_\leftarrow\exp[-\int_a^b dt\,F(t)]=1$, which is obvious since it clearly equals 1 when $a=b$, and its derivative with respect to b is zero. Note that of course A and $N(\tau)$ are understood as expanded in powers of $\tilde{R}$.

[15] See Eqs. (46) and (47) of Ref. 3.

[16] Note that the interactions V_{ij} are of order $\mathcal{V}^{-1}$, and not of order $\mathcal{V}^{-2}$ as misstated by Fano (Ref. 5); to obtain a correct density expansion, the graph components not connected to the radiator must first be eliminated, for otherwise they lead to divergences as the bulk limit is taken (for instance, we would get terms of the form $\sum_{i<j<k}\langle f_{si}f_{jk}\rangle\sim N^3\mathcal{V}^{-2}\rightarrow\infty$). Fano's density expansion is therefore incorrect, but this does not affect the first-order term, which is the one of main interest.

[17] See, for instance, R. J. Glauber [Phys. Rev. 131, 2766 (1963)] for a discussion of complete sets of wave packets.

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